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REPORTS OF THE HYDROCARBON RESEARCH GROUP.

Foreword.

The Hydrocarbon Research Group of the Institute of Petroleum has continued the work originally sponsored by the Ministry of Supply during the period 1939–44.

During the early years of the War it was necessary to devise methods for the rapid analysis of hydrocarbon mixtures. Attention was directed to the development of spectroscopic techniques, and for this purpose specimens of hydrocarbons of guaranteed purity were required. Since relatively few pure hydrocarbons were available in this country, the synthesis of a selected number was undertaken by groups of research workers at Bedford College, at Birmingham University, and at the Dyson Perrins Laboratories. The programme of work was co-ordinated with similar work in the petroleum industry by a sub-committee of the Technical Advisory Committees of the Ministry of Aircraft Production. The work of this committee has been continued by the Hydrocarbon Research Group, and the funds which have been provided by the sponsoring companies have been used to further the development of spectroscopic techniques and to maintain research work in the field of hydrocarbon chemistry.

Although the reports of the Hydrocarbon Research Group are available to members in the Institute's library, much of the earlier work has not been published. It is proposed to publish all future work in the *Journal of the Institute of Petroleum* and to hold meetings at frequent intervals at which the work of the various panels of the group (Hydrocarbon Synthesis Panel, Spectroscopic Panel, and Mass Spectrometry Panel) will be described and discussed.

In order to facilitate the publication of future work it has been decided to publish in report form the past work of the Research Groups. The three reports which follow are the first of this series and deal with the synthesis of various hydrocarbons carried out during the period 1939–44. At this time the facilities available to the various workers were limited—adequate fractionation equipment was not available—and the syntheses were therefore devised to eliminate possible side reactions and re-arrangements. The hydrocarbons so obtained were used to establish the reference spectra required for the analysis of complex mixtures and also for the studies of the relationships between spectra and structure. These studies will be published in a subsequent report of the group. Before so doing, however, it is necessary to place on record the methods by which the hydrocarbons were synthesized and the proof of the structures assigned to them. No apology is considered necessary for publishing at this time work originally reported in 1943–44, for the reports contain much that is of great interest both to organic chemists and petroleum technologists. Moreover, they illustrate the valuable contribution made by academic workers to the national effort—a contribution which in many cases has been too little publicized, but which is of increasing importance in our national recovery.

Frank Morton,
Chairman, Research Committee.

GENERAL INTRODUCTION TO PREPARATION OF HYDROCARBONS.

By M. M. Jamison, M. S. Lesslie, and E. E. Turner.

The present communication, the manuscript of which was completed in its present form on July 26, 1944, describes work done by the authors during their war-time evacuation from Bedford College, London, to the University Chemical Laboratory, Cambridge. The hydrocarbons were prepared for examination by infra-red absorption spectroscopy mainly by Dr G. B. B. M. Sutherland. Although the present account gives little idea of the labour involved in the preparation of pure hydrocarbons, it will provide authenticity for the materials upon which the spectroscopic measurements, when published, were made.

Part of the expenses for materials was defrayed by the Ministry of Aircraft Production.

The experimental work described in the following pages was carried out by the three authors.

Possible and feasible syntheses were thought out, and the one chosen selected on the basis of :—

(1) availability of starting-out material which could be purified with confidence, *i.e.*, knowing its chemical origin, and making use wherever possible of solid derivatives;

(2) possibility of purifying any intermediates *via* solid derivatives;

(3) use of reactions and reagents which experience has shown are unlikely to cause complications, *e.g.*, reducing action by Grignard reagents, molecular rearrangements, and so on. In this connexion the publications of Whitmore and his collaborators have proved invaluable.

In this way the saturated hydrocarbons finally obtained were expected to contain as impurities only by-products with much lower or much higher boiling points. No reliance was placed on elaborate fractional distillation as a method of purification, as we had neither the quantities of material nor the apparatus necessary for this purpose. Purity of product was based on pedigree. Justification for our procedure was provided by refractive-index data, and by the fact that the infra-red absorption curves were sharp. Frequently fractions boiling as much as 0·5° on either side of the fraction selected as the pure hydrocarbon gave spectra identical with that of the latter.

Iodine and sulphonic acids have usually been preferred by modern workers for the dehydration of alcohols to olefins. In our first syntheses we used iodine, but later gave it up in favour of naphthalene-β-sulphonic acid, because we found that the olefin mixture persistently retained traces of iodine, apparently in a combined condition, and that they poisoned the platinum oxide catalyst. When iodine was used it was found necessary

to shake the olefin, previously washed with alkali to remove visible iodine, with zinc dust and alkali for about an hour.

The products of reduction of olefins with Adam's platinum oxide catalyst in glacial acetic acid frequently contained small amounts of unchanged olefin, and were accordingly shaken vigorously with several successive small amounts of concentrated sulphuric acid for a few minutes, with cooling, until sulphuric acid no longer became coloured. Prolonged action of sulphuric acid was avoided.[1] The washed paraffins were then distilled several times over sodium, usually through an 8-in glass Dufton column, arranged to allow of a small amount of head reflux.

During the first part of our work we had no access to standard thermometers, and "uncorr" boiling points were taken on short unstandardized Anschütz thermometers. "Corr" values were observed with short thermometers recently standardized by the National Physical Laboratory. In all cases, temperatures are meant to indicate range of boiling point of the sample actually examined by the spectroscopists rather than the true boiling point under rigid vapour–liquid equilibrium conditions. Nevertheless, the accuracy of our boiling-point determinations left no doubt that in one or two cases of hitherto unknown hydrocarbons the "calculated" boiling points of Francis [2] were inaccurate, although they constituted a useful guide.

It may be noted that of the eighteen isomeric octanes, one, 3 : 4-dimethylhexane, and of the nonanes, four, viz., 3 : 4-dimethylheptane, 3 : 5-dimethylheptane, 2 : 3 : 4-trimethylhexane, and 2 : 2 : 3 : 4-tetramethylpentane, contain two asymmetric carbon atoms. It would be expected, therefore, that synthesis under different conditions of any of these compounds would give rise to unequal amounts of two racemic forms. It will be interesting to note, when large quantities of any of these hydrocarbons are distilled, if a separation into two forms (in the case of 3 : 5-dimethylheptane into *dl*- and *meso*-forms) is observed (compare the experimental observations on mixtures of diastereoisomeric esters made by Bailey and Hass).[3]

2 : 3-*Dimethylbutane.*

Dimethyl*iso*propylcarbinol was prepared by treating *iso*propyl magnesium bromide with acetone.[4] The yield of carbinol, b.p. 120° to 121°, was 72 per cent.

Dehydration with iodine gave a hexene mixture boiling up to 75°, and hydrogenation of this (acetic acid–platinum oxide) gave 2 : 3-dimethylbutane, b.p. 57·9° to 58·1°/770 mm uncorr, n_D^{20} 1·3755.

Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg [17] prepared the above carbinol from ethyl *iso*butyrate and methyl magnesium iodide: it had b.p. 110° to 119° as they used it for dehydration with oxalic acid. Their 2 : 3-dimethylbutane (made using a nickel catalyst) had b.p. 58·1°/760 mm and n_D^{20} 1·3751.

Brooks, Howard, and Crafton [5] record b.p. 57·999°/760 mm and n_D^{20} 1·37490.

2 : 2-*Dimethylpentane.*

Dimethyl-*n*-propylcarbinol was obtained in 61 per cent yield, b.p. 123° to 124°/767 mm, from acetone and *n*-propyl magnesium bromide.

Deschamps [6] by the same method obtained a 50 per cent yield, b.p. 122·5° to 123·5°/762 mm.

2-Chloro-2-methylpentane was obtained from the carbinol in 67 per cent yield, b.p. 35°/31 mm. Deschamps found b.p. 50° to 53°/41 mm. The chlorine atom was replaced by a methyl group as follows : 100 g of chloro-compound was placed in an all-glass apparatus with efficient condensing arrangements and filled with moving nitrogen. To it were added during 2 hr 90 g of zinc dimethyl. The mixture was warmed to 60° to 70° for 30 min and then treated with water and dilute acid. The hydrocarbon layer was separated and found to boil at 78° to 81°/767·5 mm (37 g, 45 per cent yield). To remove traces of unsaturated hydrocarbons it was extracted five times with sulphuric acid, washed with water, dried over calcium chloride, and fractionated. The pure 2 : 2-dimethylpentane had b.p. 79·0° to 79·4°/766 mm corr n_D^{20} 1·3828.

Edgar, Calingaert, and Marker [7] by the interaction of *tert*-butyl chloride and *n*-propyl magnesium bromide in presence of mercuric chloride, obtained 2 : 2-dimethylpentane, b.p. 78·2° to 79·5°/760 mm, n_D^{20} 1·38233. Marker and Oakwood,[8] from similar materials but replacing mercuric chloride by cuprous iodide, obtained 2 : 2-dimethylpentane with b.p. 79·0°/760 mm and n_D^{20} 1·3825. Soroos and Willis [9] working similarly but with no catalyst, recorded for their dimethylpentane, b.p. 78·7° to 79°/760 mm and n_D^{20} 1·3822.

3 : 3-*Dimethylpentane.*

Methyldiethylcarbinol was prepared by the action of ethyl magnesium bromide on ethyl acetate.[10] It was converted into the corresponding chloride as described by Schreiner.[11] The chloride was added to ethereal methyl magnesium iodide (3 mol). A vigorous reaction began and was completed by heating under reflux for 2 hr. The mixture was then distilled, first from a water-bath and then from a fusible metal bath, the fraction boiling at 50° to 70° being collected. After being extracted with several successive portions of concentrated sulphuric acid, washing, and drying, it was fractionated. The 3 : 3-dimethylpentane had b.p. 86·0° to 86·5°/771 mm corr, n_D^{20} 1·3913.

Smittenberg, Hoog, Moerbeck, and v.d. Zijden [12] found b.p. 86·10° and n_D^{20} 1·39092.

2 : 4-*Dimethylpentane.*

Pure di-*iso*propylcarbinol (see note on page 603) was converted into 3-bromo-2 : 4-dimethylpentane by the method of *Organic Syntheses, Collected*, Vol. I, p. 25. The bromide, b.p. 42°/12 mm (yield, 89 per cent), was allowed to react with excess of magnesium in ether, the process being completed at the b.p. The mixture was treated with water and dilute acid and then worked up normally. Pure 2 : 4-dimethylpentane was obtained, b.p. 81° to 82°/779 mm uncorr, n_D^{20} 1·3828.

Edgar, Calingaert, and Marker [13] found b.p. 80·8°/760 mm and n_D^{20} 1·3823. Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg [17] gave b.p. 80·8°/760 mm and n_D^{20} 1·3822.

3-*Ethylpentane.*

The method described by Edgar, Calingaert, and Marker [7] was used : ethyl magnesium bromide and ethyl propionate to triethylcarbinol, de-

hydration with iodine, and hydrogenation of the olefin in presence of glacial acetic acid and platinum oxide.

The ethyl propionate, b.p. 98° to 99°/760 mm, was obtained from fractionated propionic acid. The carbinol, obtained in 70 per cent yield, had b.p. 135° to 142°. The olefin mixture boiled at 93° to 98°. Hydrogenation was difficult, probably owing to the presence of combined iodine, and it was necessary to remove unsaturated products from the paraffin before distilling it. The 3-ethylpentane obtained had b.p. 92·5° to 93·5°/766 mm corr, n_D^{20} 1·3920.

Edgar and Calingaert [15] found n_D^{20} 1·39366. Brooks, Howard, and Crafton [5] found b.p. 93·473°/760 mm, n_D^{20} 1·39337.

3-*Methylheptane.*

Methyl *n*-butyl ketone was prepared from α-*n*-butylacetoacetic ester in the usual manner. The ketone was added to 1·5 mol of ethereal ethyl magnesium bromide. The 3-methylheptan-3-ol obtained by usual procedure had b.p. 161° to 162°/752 mm uncorr (yield, 78 per cent). The carbinol was dehydrated by means of iodine, the olefin being freed from traces of iodine, by prolonged shaking with zinc dust and aqueous alkali. Hydrogenation was effected with hydrogen–platinum oxide–glacial acetic acid. Traces of non-hydrogenated material were removed with concentrated sulphuric acid, and after being washed the 3-methylheptane was fractionated over sodium, when it had b.p. 118·2° to 119·2°/771 mm corr, and n_D^{20} 1·3988.

Smittenberg, Hoog, and Henkes [16] gave b.p. 119·1°/760 mm and n_D^{20} 1·3988, whilst Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg,[17] who also worked through 3-methylheptan-3-ol, but prepared it from methyl ethyl ketone, gave for 3-methylheptane the constants: b.p. 118·9°/760 mm and n_D^{20} 1·3986.

4-*Methylheptane.*

4-Methylheptan-4-ol was prepared by treating *n*-propyl magnesium bromide with methyl acetate.[18] The carbinol was dehydrated by means of iodine, and the resulting olefin, b.p. 116° to 124°/752 mm, hydrogenated (platinum oxide–acetic acid). The 4-methylheptane obtained had b.p. 118·2° to 118·7°/764 mm corr and n_D^{20} 1·3983.

Edgar and Calingaert [15] gave: b.p. 118·0° and n_D^{20} 1·398.

2 : 2-*Dimethylhexane.*

2-Methylhexan-2-ol was prepared by adding acetone to *n*-butyl magnesium bromide, using normal methods. The carbinol, b.p. 135° to 145°, was shaken with concentrated hydrochloric acid until converted into 2-chloro-2-methylhexane, and the latter, after distillation under reduced pressure, allowed to react with methyl magnesium iodide (2 mol), the reaction being completed by heating under reflux overnight. Addition of ice and then dilute acid, followed by normal procedure, gave 2 : 2-dimethylhexane, b.p. 107·0° ±0·5°/760 mm corr, n_D^{20} 1·3940.

Noller [19] who obtained the hydrocarbon from zinc di-*n*-butyl and *tert*-butyl chloride, found b.p. 106° to 107° and n_D^{20} 1·3931.

3-*Ethylhexane*.

Diethyl-*n*-propylcarbinol, obtained in 88 per cent yield, b.p. 74°/18 mm by the action of ethyl magnesium bromide on methyl *n*-butyrate [20] (*n*-butyric acid, a commercial pure material, was fractionated and esterified with methyl alcohol) was dehydrated by means of iodine. The olefin, b.p. 116° to 123°, mainly at 121°/760 mm was hydrogenated in glacial acetic acid. The 3-ethylhexane obtained after washing with concentrated sulphuric acid had b.p. 118·4° to 119·4°/758 mm corr and n_D^{20} 1·4020.

Edgar and Calingaert [21] found b.p. 118·8° and n_D^{20} 1·4016.

2-*Methyl*-3-*ethylpentane*.

Diethyl*iso*propylcarbinol, b.p. 56° to 57°/11 mm, was prepared by adding methyl *iso*butyrate to excess of ethyl magnesium bromide. Pure commercial *iso*butyric acid was fractionated, the fraction b.p. 154° to 154·5°/772 mm being collected. It was converted into the acid chloride by the method of Smith and Lewcock [22]: the chloride had b.p. 93·3° to 93·5°/774 mm. It was allowed to react with excess of methyl alcohol, and the methyl ester obtained fractionated. The fraction, b.p. 92·5° to 92·8°/772 mm was used. The carbinol, obtained in 86 per cent yield, was converted into the corresponding bromide by means of phosphorus tribromide, and the bromide (b.p. 66° to 67°/11 mm, yield 93 per cent) was allowed to react with excess of magnesium in presence of ether. The interaction was completed by prolonged heating under reflux, and the reaction mixture was treated with ice and then dilute acid. Normal subsequent procedure gave 2-methyl-3-ethylpentane, b.p. 113° to 114°/761·5 mm corr, n_D^{20} 1·4050.

Edgar and Calingaert [21] found b.p. 114·0°/760 mm and n_D^{20} 1·4016.

3-*Methyl*-3-*ethylpentane*.

Methyldiethylcarbinol b.p. 42°/11 mm, was obtained in 77 per cent yield by the interaction of ethyl acetate with ethyl magnesium bromide.[23] It was converted into the corresponding chloride by the method of Schreiner,[24] and the chloride was added to zinc diethyl.[17] The 3-methyl-3-ethylpentane finally obtained had b.p. 117·0° to 118·6°/758·5 mm corr and n_D^{20} 1·4086.

Smittenberg, Hoog, and Henkes [16] recorded b.p. 118·4°/760 mm and n_D^{20} 1·4081.

2-*Methyloctane*.

(*a*) *sec*-Octyl alcohol. The redistilled commercial material was converted into the hydrogen phthalate by the method of Levene and Mikeska.[25] After crystallization from light petroleum (b.p. 60° to 80°) it had m.p. 59° to 60° (*Organic Syntheses, Collected*, Vol. I, p. 418, gives m.p. 55°) Saponification of the ester gave pure *sec*-octyl alcohol, b.p. 179·5° to 180°/764 mm uncorr.

(*b*) Methyl *n*-hexyl ketone. Oxidation of the alcohol by means of potassium dichromate and diluted sulphuric acid, followed by purification of the ketone through the sodium bisulphite compound, gave methyl *n*-hexyl ketone, b.p. 172° to 172·5°/762 mm uncorr. Henderson, Henderson,

and Heilbron [26] gave b.p. 172° to 173°/767 mm for the ketone purified through the semicarbazone.

(*c*) Dimethyl-*n*-hexylcarbinol. Interaction of the ketone with ethereal methyl magnesium bromide gave the carbinol in 88 per cent yield, b.p. 81° to 83°/16 mm. Whitmore and Southgate,[27] employing methyl magnesium chloride, gave b.p. 82° to 85°/20 mm (yield, 85 per cent).

(*d*) 2-Methyloctenes. The carbinol was distilled with a little naphthalene-β-sulphonic acid. The distillate was twice again similarly treated. Whitmore and Southgate [27] used iodine as dehydrating catalyst.

(*e*) 2-Methyloctane. The dried nonene mixture was hydrogenated in glacial acetic acid in presence of platinum oxide, and gave 2-methyloctane, b.p. 143·8° to 144·4°/763 mm uncorr, n_D^{20} 1·4030.

Whitmore and Southgate [27] found b.p. 142·80°/760 mm and n_D^{20} 1·40285 for 2-methyloctane obtained by hydrogenation of the nonene mixture in presence of nickel, and b.p. 142·8°/760 mm, n_D^{20} 1·4030 for 2-methyloctane derived from dimethyl-*n*-hexylcarbinol *via* the iodide, the latter being reduced with zinc and alcohol.

3-*Methyloctane.*

Methylethyl-*n*-amylcarbinol was prepared by two different methods :—

Method 1. *sec*-Butyl alcohol, b.p. 101°/765 mm, obtained by the fractionation of the pure commercial material, was oxidized to methyl ethyl ketone as follows : A solution of 294 g (1-mol) of potassium dichromate and 400 g (4 mol) of concentrated sulphuric acid in 2 litres of water was gradually added to 222 g (3 mol) of *sec*-butyl alcohol, kept well shaken and cooled below about 25°. This operation completed (30 to 40 min), the methyl ethyl ketone and some water (182 g in all) were removed by distillation and the wet ketone dried over several successive quantities of anhydrous sodium sulphate and finally over potassium carbonate; 82 g of pure ketone, b.p. 78° to 82°, mainly 79° to 80°/757 mm were obtained.

n-Amyl alcohol, purified through the hydrogen phthalate, was converted into *n*-amyl bromide by the general method described in *Organic Syntheses*, Vol. I.

Methyl ethyl ketone (1 mol) was gradually added to ethereal *n*-amyl magnesium bromide (1·2 mol) and the product worked up in the usual way. 74 g (51 per cent yield) of methylethyl-*n*-amylcarbinol, b.p. 83° to 85°/18 mm were obtained.

Method 2. *n*-Butyl alcohol, b.p. 117·2°, obtained by fractionation of the pure commercial material, was converted into *n*-butyl bromide by the method described in *Organic Syntheses*. The bromide had b.p. 101° to 102°.

Methyl *n*-amyl ketone was prepared by the method described in *Organic Syntheses, Collected*, Vol. 1, pp. 248 and 351, and was obtained in 45 per cent yield, b.p. 148·5° to 149·5°/764 mm. The ketone was allowed to react with ethyl magnesium bromide.[28] The yield of methylethyl-*n*-amylcarbinol was 86 per cent, b.p. 83°/18 mm.

Methylethyl-*n*-amylcarbinol was dehydrated with naphthalene-β-sulphonic acid and gave a product boiling up to 150°. 3-Methyloctane was obtained by hydrogenating the nonene mixture in glacial acetic acid in presence of platinum oxide. Two separate preparations gave (*a*) : b.p.

144·0° to 145·0°/756 mm uncorr, n_D^{20} 1·4069, and (*b*) 143·9° to 144·9°/756 mm uncorr, n_D^{20} 1·4062.

Levene and Marker [29] from the Grignard reagent derived from a (+) 1-bromo-3-methyloctane, obtained a lævorotatory 3-methyloctane with b.p. 143°, and the same authors [121] obtained by a similar method, from a (+)-5-bromo-3-methyloctane, a dextrorotatory 3-methyloctane, b.p. 143° to 144°/760 mm.

4-*Methyloctane.*

Methyl *n*-propyl ketone, purified through the semicarbazone melting at 111° to 112°, boiled at 101° to 103°. Interaction of the ketone with *n*-butyl magnesium bromide, prepared from *n*-butyl bromide, b.p. 101° to 102° (ex fractionated *n*-butyl alcohol, b.p. 117·2°) gave methyl-*n*-propyl-*n*-butylcarbinol, b.p. 82° to 83°/18 mm in 66 per cent yield. Whitmore and Woodburn,[30] using the same method, recorded b.p. 78·5° to 79·5°/15 mm and a 68 per cent yield.

Dehydration of the carbinol (28 g) with naphthalene-β-sulphonic acid gave 16·5 g of nonene mixture, b.p. 135° to 145°/761 mm, mainly 143° to 144°. Midgley and Henne [31] obtained 4-methyloct-4-ene from isoprene, sodium, and ethyl bromide, and recorded a b.p. of 136° to 144°, mainly 139°. Hydrogenation of our nonene mixture in glacial acetic acid in presence of platinum oxide gave a product, which, after fractionation, led to 10·5 g of 4-methyloctane, b.p. 142·9° to 143·0°/763 mm uncorr, n_D^{20} 1·4063.

Clarke,[32] who reduced a nonene mixture with hydrogen and nickel, found b.p. 141·7° to 141·9°/771 mm. For the 4-methyloctane present in Oklahoma petroleum, White and Glasgow [33] found b.p. 142·433°.

It may also be noted that Levene and Marker,[29] who found a lævorotatory specimen of 4-methyloctane to boil at 141°/760 mm, later described a "5-methyloctane" boiling at 53°/25 mm.[29]!

2 : 2-*Dimethylheptane.*

Methyl *n*-amyl ketone was obtained by the method of *Organic Syntheses, Collected*, Vol. I, pp. 248 and 351. The yield of ketone, b.p. 148·5° to 149·5°/764 mm was 62 per cent on the *n*-butylacetoacetic ester (b.p. 112° to 113°/16 mm) and 45 per cent on the acetoacetic ester used.

Dimethyl-*n*-amylcarbinol was prepared by the action of methyl magnesium bromide on methyl *n*-amyl ketone, and was obtained in 84 per cent yield, b.p. 66°/11 mm. Masson,[34] who made the carbinol from methyl magnesium iodide and ethyl *n*-hexoate, recorded b.p. 162°.

2-Chloro-2-methylheptane was made by shaking the carbinol with concentrated hydrochloric acid and calcium chloride. It had b.p. 52°/11 mm and was obtained in 84 per cent yield. Muset [35] prepared the chloride by treating the carbinol with acetyl chloride.

Interaction of the chloride with zinc dimethyl resulted in a violent detonation, and the following method was therefore substituted: To a Grignard reagent prepared from 36 g of magnesium (1·7 atoms) and 213 g (1·7 mol) of methyl iodide and cooled to 0° was added 107 g (1 mol) of 2-chloro-2-methylheptane. When addition was complete, the mixture was allowed to warm up and was then heated under reflux for a day.

Usual working-up gave a crude hydrocarbon, b.p. 126° to 131°/776 mm. This was extracted with small quantities of sulphuric acid until free from unsaturation, washed, dried, and fractionated. The 2 : 2-*dimethylheptane* obtained had b.p. 132·6° to 133·4°/774 mm corr, n_D^{20} 1·4015.

Morton and Fallwell [36] reported that sodium amyl reacted with *tert*-butyl bromide to give a 5·5 per cent yield of 2 : 2-dimethylheptane, but no other details were mentioned.

2 : 3-*Dimethylheptane.*

Methyl *iso*propyl ketone was prepared by the method of *Organic Syntheses*, Vol. XIII, p. 68, from *tert*-amyl alcohol which had previously been fractionated and then had b.p. 101°/752 mm. The yield of ketone, b.p. 94° to 96°, varied within a few grams around the figure given in *Organic Syntheses*.

The ketone (1 mol) was added to 1·2 mol of ethereal magnesium *n*-butyl bromide, the product being worked up in a normal manner. The yield of methyl*iso*propyl-*n*-butylcarbinol, b.p. 75° to 77°/16 mm was 54 per cent. Whitmore and Southgate,[27] using a similar method, found b.p. 75° to 78°/16 mm and yield 65 per cent.

The carbinol (50 g) was dehydrated with naphthalene-β-sulphonic acid, 39 g of nonene mixture, b.p. 139° to 143°, being obtained. Whitmore and Southgate recorded b.p. 135° to 140°/735 mm. The nonene mixture was hydrogenated in glacial acetic acid in presence of platinum oxide. The 2 : 3-dimethylheptane obtained, after repeated fractionation, had b.p. 140·0° ±0·05°/757 mm corr, n_D^{20} 1·4090. Yield of pure material, 23 g.

Whitmore and Southgate recorded b.p. 140·65°/760 mm and n_D^{20} 1·40850 for 2 : 3-dimethylheptane prepared by hydrogenation of their nonene mixture (obtained by iodine dehydration of the carbinol) in presence of nickel–alumina.

2 : 4-*Dimethylheptane.*

Methyl *iso*butyl ketone was prepared from acetoacetic ester in the usual manner. Interaction with *n*-propyl magnesium bromide [37] gave methyl-*n*-propyl*iso*butylcarbinol, b.p. 174° to 176°/764 mm in 71 per cent yield.

The carbinol was dehydrated with naphthalene-β-sulphonic acid, and the unsaturated hydrocarbon was reduced in glacial acetic acid with hydrogen and platinum oxide. The 2 : 4-dimethylheptane obtained had b.p. 133·3° to 133·5°/758 mm corr, n_D^{20} 1·4030.

Tuot [38] gives b.p. 130°/749 mm and n_D^{20} 1·4023.

2 : 5-*Dimethylheptane.*

Interaction of 82 g (1·1 mol) of methyl ethyl ketone (obtained from *sec*-butyl alcohol as described elsewhere) and 1·33 mol of *iso*amyl magnesium bromide in ethereal solution gave a 75 per cent yield of methylethyl*iso*amylcarbinol, b.p. 73° to 74°/13 mm.

Meyer and Tuot,[39] using the same general method, found b.p. 85°/25 mm for the carbinol, but recorded no yield.

The carbinol (119 g) was dehydrated (two successive operations) with naphthalene-β-sulphonic acid. The washed and dried nonene mixture boiled at 120° to 140°. Fractionation gave 31 g, b.p. 137·0° to 137·4°/762

mm uncorr, and 45 g b.p. 134° to 141°/762 mm (redistillation of combined fractions). These two fractions were hydrogenated (glacial acetic acid-platinum oxide) separately. Fractionation of the two saturated hydrocarbons produced showed them to be identical, and the corresponding best fractions were mixed and the whole refractionated. The pure 2 : 5-dimethylheptane obtained had b.p. 135·6° to 135·8°/753 mm corr, n_D^{20} 1·4044.

Meyer and Tuot [39] dehydrated their carbinol with copper sulphate. Their 2 : 5-dimethylhept-4-ene had b.p. 137°/747 mm and by catalytic hydrogenation they obtained 2 : 5-dimethylheptane, b.p. 133°/741 mm, n_D^{20} 1·4033.

Edgar and Calingaert [15] recorded b.p. 135·9°.

2 : 6-*Dimethylheptane.*

*iso*Butyraldehyde was prepared from previously fractionated *iso*butyl alcohol and purified through the sodium bisulphite compound.

75 g (1 mol) of *iso*butyraldehyde were gradually added to a Grignard reagent made from 240 g (1·5 mol) of *iso*amyl bromide (previously fractionated) and magnesium, of which 73 g (3 atoms) were used, excess being removed by decantation before use. Normal working up gave 142 g (94 per cent yield) of *iso*propyl*iso*amylcarbinol, b.p. 65° to 75°/13 mm (mainly, 73° to 74°/13 mm). Redistillation gave 120 g (80 per cent yield) of pure carbinol, b.p. 178° to 182°/779 mm.

Tuot,[40] using the same starting materials, found b.p. 88°/25 mm.

*iso*Propyl*iso*amylcarbinol proved to be very difficult to dehydrate. It remained almost unaffected after prolonged boiling in presence of naphthalene-β-sulphonic acid, and was recovered by distillation. A little iodine was added and the mixture again boiled. Very little dehydration occurred and the iodine colour disappeared. The carbinol was distilled and again heated with naphthalene-β-sulphonic acid. After several hours 20 cc of nonene mixture were obtained from 115 g of carbinol, the remainder of the product polymerizing. The nonene mixture was boiled under reflux with zinc dust and dilute sodium hydroxide to remove traces of iodine, and finally hydrogenated in glacial acetic acid in presence of platinum oxide. Fractionation of the nonene obtained gave 1 cc, b.p. 134·5° to 135·5°/766 mm, n_D^{20} 1·4096.

The carbinol (1 mol) was therefore converted into 3-bromo-2 : 6-dimethylheptane by means of phosphorus tribromide (2 to 3 mol), starting in the cold and finishing at 100. The yield of bromo-compound, b.p. 76° to 77°/15 mm, was 68 per cent.

The bromo-compound was heated under reflux for 1 hr with excess of magnesium which had previously been activated with ethyl bromide. The mixture was treated with water and dilute acid and the hydrocarbon isolated in the usual manner. It had b.p. 125° to 150°, and since it contained unsaturated material it was hydrogenated in glacial acetic acid in presence of platinum oxide. Fractionation gave pure 2 : 6-dimethylheptane, b.p. 135·2° to 135·6°/766 mm corr, n_D^{20} 1·4010.

White, Rose, Calingaert, and Soroos [41] for 2 : 6-dimethylheptane derived from 2 : 6-dimethylheptan-4-ol recorded b.p. 135·21° ± 0·02°/760 mm and n_D^{20} 1·40073.

3 : 3-*Dimethylheptane.*

n-Propylacetoacetic ester was obtained, b.p. 205° to 212°, in 55 per cent yield from acetoacetic ester and *n*-propyl bromide, following usual methods. Hydrolysis with dilute alkali gave a 72 per cent yield of methyl *n*-butyl ketone, b.p. 126° to 128°. *Organic Syntheses, Collected*, Vol. I, p. 351, records yield 50 per cent and b.p. 126° to 128°. Methylethyl-*n*-butylcarbinol was obtained from the ketone in 63·5 per cent yield, b.p. 68°/16 mm. Clarke [42] prepared the carbinol from methyl butyl ketone and ethyl magnesium bromide, and Whitmore and Woodburn [30] from methyl ethyl ketone and butyl magnesium bromide. The latter authors recorded b.p. 65·2° to 65·8°/15 mm.

3-Chloro-3-methylheptane was prepared by shaking the carbinol with concentrated hydrochloric acid and saturating with calcium chloride. It was obtained in 72 per cent yield, b.p. 50° to 54°/16 mm. Whitmore and Woodburn [30] saturated the carbinol with hydrogen chloride and recorded b.p. 55·0°/15 mm.

Conversion of the chloro-compound into 3 : 3-dimethylheptane was effected as follows :—

66 g of the chloro-compound were added to a Grignard reagent prepared from 18 g of magnesium (1·5 atoms) and 74 g of methyl bromide. The reaction was vigorous, and after 2 hr standing the mixture was heated under reflux for 20 hr, cooled, and treated with ice and then dilute acid. Normal working-up gave a crude hydrocarbon boiling at 125° to 132°/765 mm. This was repeatedly extracted with small quantities of concentrated sulphuric acid until free from unsaturation, then washed, dried, and fractionated. A 15 per cent yield of almost pure 3 : 3-dimethylheptane was obtained, and of this the best fraction (6 cc) had b.p. 136·0° to 136·6°/765 mm corr, n_D^{20} 1·4080. Noller,[19] from *tert*-amyl chloride and zinc di-*n*-butyl in tetralin, obtained 3 : 3-dimethylheptane with b.p. 137° to 138°, n_D^{20} 1·4095. Marker and Oakwood [43] from *tert*-amyl chloride and *n*-butyl magnesium bromide in presence of cuprous iodide isolated 3 : 3-dimethylheptane with b.p. 137·2°/760 mm and n_D^{20} 1·4087.

Campbell and Eby [44] (*a*) from 3 : 3-dimethylhept-4-yne obtained by reduction the heptane boiling at 135°/735 mm, n_D^{20} 1·4078 and (*b*) from *tert*-amyl bromide and *n*-butyl magnesium bromide obtained 3 : 3-dimethylheptane in poor yield, b.p. 136°/745 mm, n_D^{20} 1·4084.

3 : 4-*Dimethylheptane.*

Methylethylacetic acid was prepared by the method of *Organic Syntheses, Collected*, Vol. I, p. 361. The *sec*-butyl bromide used, b.p. 91°, was prepared from fractionated *sec*-butyl alcohol. The yield of acid in the last stage was 60 per cent.

Methylethylacetamide was prepared from the acid *via* the acid chloride. This, when shaken in the cold with concentrated aqueous ammonia, gave the amide, which, after being crystallized first from alcohol and then from benzene, melted at 112° to 113°. Schleuble and Löbl [45] found m.p. 112°. In attempting to circumvent the old process of treating the acid chloride with aqueous ammonia, with its tedious working-up, we made the somewhat interesting observation that the chloride does not react with dry ammonia gas in dry ethereal solution. The amide was

converted into *n*-propyl *sec*-butyl ketone as follows: A Grignard reagent (3 mol) was prepared from 48 g of magnesium and 246 g of *n*-propyl bromide. It was stirred, and 68 g (1 mol) of methylethyl acetamide were gradually added, stirring being then continued for a further 21 hr. Normal working-up afforded 41 g of ketone, b.p. 152·5° to 155·5°, *i.e.*, 49 per cent of the possible yield. The b.p. 154°/73 mm recorded by Whitmore and Block [46] must be a misprint. A Grignard reagent was prepared from 16 g (2 atoms) of magnesium and 64 g of methyl bromide. To this, 40 g (1 mol) of the ketone was added. Decomposition by the usual method gave 40 g of methyl-*n*-propyl-*sec*-butylcarbinol (yield, 90 per cent), b.p. 172° to 178°/768 mm. The carbinol was distilled slowly from naphthalene-β-sulphonic acid, the water separated, and the process repeated three times. The nonene mixture boiled up to 145°.

The nonene mixture was hydrogenated in glacial acetic acid in presence of platinum oxide. The hydrocarbon obtained was freed from unsaturation by two extractions with concentrated sulphuric acid, and finally fractionated. The 3 : 4-dimethylheptane obtained had b.p. 139·8° to 140·6°/761 mm corr, n_D^{20} 1·4114.

4 : 4-*Dimethylheptane.*

Method 1. Di-*n*-propylcarbinol was obtained in 78 per cent yield, b.p. 57°/12 mm, by the interaction of *n*-butyraldehyde and 1·2 mol of *n*-propyl magnesium bromide. The carbinol (182 g; 3 mol) was gradually treated with a solution of 242 g (1·5 mol) of potassium dichromate and 220 g (about 4 mol) of concentrated sulphuric acid in 1650 cc of water. When the oxidation was complete, the mixture was distilled in steam, the ketone separated, washed with dilute sodium carbonate, dried, and distilled. The yield of pure ketone, b.p. 146° to 148°/765 mm was 73 per cent.

Interaction of di-*n*-propyl ketone with 1·5 mol of methyl magnesium iodide gave methyl di-*n*-propylcarbinol, b.p. 159° to 162°, in 72 per cent yield. Small amounts of di-*n*-propylcarbinol were also formed. Interaction of the chloride, prepared as above, with 2 mol of methyl magnesium iodide, gave only a poor yield of impure 4 : 4'-dimethylheptane, b.p. 132° to 133°/773 mm.

Method 2. Methyldi-*n*-propylcarbinol, b.p. 159° to 162°, was obtained in 78 per cent yield by the interaction of ethyl acetate with *n*-propyl magnesium bromide (3 mol) and was converted into the corresponding chloride by the action of concentrated hydrochloric acid, compare Halse.[18] To the freshly distilled chloride (b.p. 54° to 55°/16 mm) (71 g) zinc dimethyl (70 cc) was gradually added, with cooling. The mixture was eventually heated in boiling water and kept overnight. Water and dilute hydrochloric acid were added, the hydrocarbon layer separated, dried over calcium chloride, and distilled. It was then extracted with several successive small quantities of concentrated sulphuric acid until free from unsaturation, washed, dried, and distilled. 7 cc of 4 : 4-dimethylheptane were obtained, b.p. 135·0° to 135·7°/773 mm corr n_D^{20}, 1·4078.

3-*Ethylheptane.*

Diethyl ketone, the commercial pure material, was fractionated and added to *n*-butyl magnesium bromide,[47] when diethyl-*n*-butylcarbinol, b.p. 180° to 182° was obtained in 76 per cent yield.

Dehydration of the carbinol with naphthalene-β-sulphonic acid gave an olefin mixture which was hydrogenated in glacial acetic acid in presence of platinum oxide. The 3-ethylheptane formed had b.p. 142·6° to 143·0/766 mm corr, n_D^{20} 1·4091. Whitmore and Southgate [27] gave b.p. 143·1°/760 mm and n_D^{20} 1·4090.

2 : 2 : 5-Trimethylhexane.

A pure commercial sample of *iso*amyl alcohol was fractionated, the portion boiling at 121·8° to 122·4°/774 mm being converted into the bromide by the method of *Organic Syntheses*, Vol. I, p. 4. *tert*-Butyl alcohol was purified by freezing and filtering and converted into the chloride. The latter was added (145 g) to *iso*amyl magnesium bromide, the mixture being then heated under reflux for 6 hr. The semi-solid mixture was then distilled from a bath until the temperature of the latter rose to 230°. The distillate was fractionated. The 2 : 2 : 5-trimethylhexane obtained had b.p. 124° to 125°/774 mm and n_D^{20} 1·4002.

Campbell [48] found b.p. 122·9° to 123·0°/736 mm and n_D^{20} 1·3997.

2-Methyl-3-ethylhexane.

*iso*Butyramide was prepared by converting *iso*butyric acid (b.p. 154°/767 mm) into the chloride by means of thionyl chloride, followed by concentrated ammonia solution. The amide, b.p. 215°, was added to 3 mol of ethereal ethyl magnesium bromide, kept stirred. The interaction was vigorous and was brought to completion by stirring for a further 23 hr. Normal working-up gave ethyl *iso*propyl ketone, b.p. 114° to 116° in 69 per cent yield.

The ketone was allowed to react with *n*-propyl magnesium bromide. The ethyl-*n*-propyl*iso*propylcarbinol obtained showed a tendency to undergo spontaneous dehydration when distilled at the ordinary pressure, but was finally isolated with b.p. 160° to 175°/777 mm. Stas,[49] who used similar procedure, found b.p. 176·5° to 177·5°/755 mm and recorded a theoretical yield.

Dehydration of the carbinol with naphthalene-β-sulphonic acid (two operations) gave a nonene mixture, b.p. 128° to 138°, and hydrogenation of this in glacial acetic acid in presence of platinum oxide gave 2-methyl-3-ethylhexane, the best fraction of which had b.p. 138·6° to 138·8°/773 mm corr, n_D^{20} 1·4134.

3-Methyl-3-ethylhexane.

Diethyl-*n*-propylcarbinol was prepared by the interaction of *n*-propyl magnesium bromide and diethyl ketone (redistilled pure commercial material; b.p. 104° to 106°) and was distilled first under reduced pressure (b.p. 68° to 72°/12 mm) and then, to remove diethylcarbinol, at the ordinary pressure. The pure carbinol, b.p. 160° to 162°/770 mm uncorr, was isolated in 70 per cent yield. Clarke and Riegel [50] gave b.p. 155° to 159°/756 mm.

The carbinol was converted into 3-chloro-3-ethylhexane by means of concentrated hydrochloric acid. The chloride had b.p. 50° to 53°/15 mm and was obtained in 70 per cent yield.

Butlerow [51] prepared the chloride by treating the carbinol with phosphorus pentachloride. The chloro-compound (120 g) was added gradually to 3 mol of ethereal methyl magnesium bromide. The mixture was then boiled under reflux for 16 hr, treated with ice and dilute acid and the hydrocarbon worked-up normally. The crude material had b.p. 120° to 140° and contained unsaturated compounds which were extracted by means of concentrated sulphuric acid. The pure hydrocarbon had b.p. 140·0° to 140·5°/765 mm corr, n_D^{20} 1·4140.

2-*Methyl*-4-*ethylhexane*.

Two syntheses were carried out :—

Method 1. Pure commercial *iso*valeric acid was dried over phosphorus pentoxide, fractionated (b.p. 176° to 178°), and converted into methyl *iso*valerate, b.p. 118° to 119°.

Interaction of the ester (1 mol) with 3 mol of ethereal ethyl magnesium bromide gave diethyl*iso*butylcarbinol in 80 per cent yield, b.p. 68° to 69°/18 mm, compare Masson.[34] The carbinol, 32 g, dehydrated in two operations with naphthalene-β-sulphonic acid, gave 27 g of nonene mixture, b.p. 128° to 139°. Hydrogenation in glacial acetic acid (platinum oxide) gave, after fractionation, 2-methyl-4-ethylhexane, b.p. 133·8° to 134·1°/767 mm corr, n_D^{20} 1·4070.

Method 2. *iso*Valeric acid (550 g) was left with 1 mol of thionyl chloride for 12 hr. The mixture was then heated at 100° for 1 hr, cooled, and added gradually to excess of concentrated ammonia and ice. The *iso*valeramide was filtered and crystallized from water, when it had m.p. 133° to 134°, subsequent crystallization from acetone not affecting this m.p. The yield of pure amide was 182 g.

The amide (1 mol) was gradually added to 3 mol of ethereal ethyl magnesium bromide, with continuous stirring, which was maintained during a further 24 hr. The mixture was worked up in a normal manner, and gave a 61 per cent yield of ethyl *iso*butyl ketone, b.p. 136° to 137°.

Beis,[52] who obtained the ketone by a similar method, found b.p. 134·5° to 135°/735 mm.

Interaction of ethyl *iso*butyl ketone (68 g) with 2 mol of ethereal ethyl magnesium bromide gave 75 g of crude diethyl*iso*butylcarbinol, b.p. 62° to 64°/12 mm. This, redistilled at ordinary pressure, was found to contain some ethyl*iso*butylcarbinol, formed by the reducing action of the Grignard reagent; 50 g of pure diethyl*iso*butyl carbinol being obtained. The carbinol was dehydrated as before, the nonene mixture boiling at 135° to 140°. On reduction it gave 2-methyl-4-ethylhexane, b.p. 134·1° to 134·4°/767 mm corr, n_D^{20} 1·4072.

4-*Ethylheptane*.

Pure commercial propionic acid was fractionated and converted into ethyl propionate, which was further fractionated. The ester was allowed to react with excess of magnesium *n*-propyl bromide. Halse [53] gives b.p. 179·5° corr. The ethyldi-*n*-propylcarbinol obtained boiled at 182° to 183°/770 mm.

Dehydration of the carbinol with naphthalene-β-sulphonic acid gave a nonene mixture, b.p. 142° to 144°/770 mm, and the latter, after hydro-

genation (glacial acetic acid–platinum oxide) gave 4-ethylheptane, b.p. 140·6° to 140·8°/766 mm corr, n_D^{20} 1·4084.

2 : 4-*Dimethyl*-3-*ethylpentane*.

Di-*iso*propyl ketone was fractionated and then converted into the semicarbazone. This, after being crystallized three times from methyl alcohol, had m.p. 153° to 154°. The semicarbazone (247 g) hydrolysed by boiling with 20 per cent hydrochloric acid, gave 138 g (84 per cent yield) of pure ketone, b.p. 127°.

Interaction of the ketone (138 g; 1 mol) with 2 mol of ethereal ethyl magnesium bromide gave 165 g of crude ethyldi-*iso*propylcarbinol boiling mainly at 65°/15 mm. Distillation of this material at the ordinary pressure gave 149 g, b.p. 160° to 177°, some low boiling material being rejected, compare Whitmore and George.[54] The carbinol was dehydrated with naphthalene-β-sulphonic acid (two operations) and gave 125 g of nonene mixture, b.p. 125° to 140°.

Hydrogenation of the nonene mixture in glacial acetic acid in presence of platinum oxide was slow, but finally led to a product which contained only small amounts of unsaturated material, these then being removed by extraction with concentrated sulphuric acid. Fractionation gave 24 cc of 2 : 4-dimethyl-3-ethylpentane, b.p. 136·6° to 137·0°/775 mm corr, n_D^{20} 1·4138.

An attempt to prepare ethyldi-*iso*propylcarbinol by the interaction of ethyl propionate and 3 mol of *iso*propyl magnesium bromide led, as was anticipated, to a poor yield (8 to 10 per cent).

Note.—For some of this work, di-*iso*propyl ketone was purified as follows, in order to make certain that it contained no unidentifiable impurities :—

Preparation of di-*iso*propyl carbinol : 256 g of sodium were added in small pieces, to a mixture of 228 g of di-*iso*propyl ketone (b.p. 121° to 124°/756 mm, 90 cm Vigreux column) and 2500 cc of absolute alcohol. The addition completed (about 1 hr) water was added and the mixture was extracted three times with ether. The combined ethereal extracts were washed with brine, dried over potassium carbonate, and distilled, when 186 g (80 per cent yield) of carbinol were obtained, b.p. 130° to 138°, mainly 135° to 136°.

A mixture of the carbinol (186 g, 1 mol) with 1 mol each of phthalic anhydride and pyridine, was heated over a free flame to 105°, when spontaneous warming set in. The mixture was heated for 2 hr in boiling water, treated with 200 cc of glacial acetic acid and then poured into 2 litres of dilute hydrochloric acid. The oil separating at once solidified. The solid was filtered and crystallized once from glacial acetic acid without being previously dried. This gave an 82 per cent yield of hydrogen phthalate, m.p. 163° to 164°. Two crystallizations of the crude hydrogen phthalate from alcohol were necessary to effect an equivalent purification, and the yield of pure ester was then only 60 per cent. (Found : C, 68·1; H, 7·6. $C_{15}H_{20}O_4$ requires C, 68·1; H, 7·6 per cent.)

A mixture of the hydrogen phthalate (353 g) with a solution of 225 g of sodium hydroxide in 1150 cc of water was boiled under reflux for 30 min, and the mixture then distilled until no more carbinol came over. The distillate was saturated with sodium chloride, separated, and the

carbinol dried over potassium carbonate and then distilled. 145 g (93 per cent yield) boiled at 137° to 139°, the great majority at 138·3° to 138·5°/753 mm uncorr.

The pure carbinol was oxidized to di-*iso*propyl ketone as follows : A solution of 141 g (1·33 mol) of potassium dichromate and 191 g (5·33 mol) of concentrated sulphuric acid in 950 cc of water was added, in 50-cc lots, to 125 g (3 mol) of carbinol in a 2-litre flask, with initial warming to 60° to start the reaction which then kept the temperature at 60° to 80°. Addition took about 1 hr. The mixture was then distilled until no more oil came over. The distillate was saturated with sodium chloride and the oily layer separated, extracted three times with brine, once with dilute sodium hydroxide and once with water. The moist ketone (108 g) was used for conversion into the semicarbazone, from which pure ketone, b.p. 125·6° to 125·8°/766 mm (uncorr) was obtained, as described above.

cis- and *trans*- 3 : 5-Dimethyl*cyclo*hexanol.

The material was obtained from two sources :—

(1) Messrs Howards. The product (2 lb) was semi-solid and was filtered at the ordinary temperature. The mother liquor was kept at 5° overnight and a second crop of solid filtered. Both solids melted at about 29° to 31° and were therefore mixed, giving in all 292 g. The mother liquor was distilled and boiled at 186° to 188·5°/751 mm.

(2) Imperial Chemical Industries Ltd.

(*a*) A series of fractions were supplied. Those having b.p. between 183·0° and 186·8° were practically solid, those having b.p. between 186·8° and 188·5° being liquid. The solid fractions all had f.p. between 32·5° and 34·5°, and mixtures had the same approximate f.p. A mixture of all the solid fractions had f.p. 33·5°.

(*b*) A series of fractions were supplied. Those having b.p. between 178·6° and 186·0° were solid. The fractions, b.p. 186·4° to 187·7°, were liquid.

(*c*) The total product of hydrogenating 5-*m*-xylenol was supplied. It was distilled through an 8-in Dufton column and boiled from 184° to 194°.

For the purpose of the present work, any sample of dimethyl*cyclo*hexanol which had a freezing point of about 30° was taken as a mixture of *cis* (Me, Me) forms, free from *trans* (Me, Me), since von Braun and Haensel [55] had established the *cis*-configuration of the solid material. The liquid portions were a mixture of both *cis* and *trans* forms. Pure *trans*-carbinol was obtained by converting the mixture into the hydrogen phthalate (by heating for 2 hr at 100° with 1 mol each of phthalic anhydride and pyridine) and saponifying the product after repeated crystallization from 90 per cent acetic acid.

cis-3 : 5-Dimethyl*cyclo*hexanone : Solid dimethyl*cyclo*hexanol (326 g), mainly one *cis* form, and containing no *trans* form, was converted into 3 : 5-dimethyl*cyclo*hexanone by adding to it gradually with shaking a solution of 248 g of potassium dichromate and 340 g of concentrated sulphuric acid in 1600 cc of water. The ketone was steam-distilled from the oxidation mixture, the distillate saturated with calcium chloride, the ketone separated, dried over potassium carbonate, and converted into

the semicarbazone. The latter, after crystallization from ethyl alcohol, had m.p. 201° to 202° (345 g). Hydrolysis with hydrochloric acid, followed by usual procedure, gave 151 g of *cis*-3 : 5-dimethyl*cyclo*hexanone, b.p. 182·9°/765 mm uncorr, and 49 g b.p. 182·9° to 184·1°.

von Braun and Haensel [55] gave m.p. 202° to 203° for the semicarbazone, and 182° to 183° for the b.p. of the pure *cis*-ketone.

trans-3 : 5-Dimethyl*cyclo*hexanone : This was obtained from *trans*-3 : 5-dimethyl*cyclo*hexanol, purified through the hydrogen phthalate. The pure ketone had b.p. 183·0°/758 mm uncorr.

1 : 3-Dimethyl*cyclo*hexane.

(1) *trans*-3 : 5-dimethyl*cyclo*hexanol (30 g), purified through the hydrogen phthalate, was dehydrated with naphthalene-β-sulphonic acid. This process was slow, but gave 21 g of crude dimethyl*cyclo*hexene, of which 18 g had b.p. 122·8° to 123·8°/749 mm uncorr. Hydrogenation in glacial acetic acid in presence of platinum oxide gave 1 : 3-dimethyl*cyclo*hexane, of which 5 cc had b.p. 118·5° to 120·5°/758 mm corr, 7 cc 120·5° to 121·0°, and 9 cc 121·0° to 121·5° corr, n_D^{20} respectively being 1·4250, 1·4251, and 1·4254.

(2) Almost pure *cis*-3 : 5-dimethyl*cyclo*hexanol, similarly treated, gave 1 : 3-dimethyl*cyclo*hexene, b.p. 121° to 123°/764 mm and thence 1 : 3-dimethyl*cyclo*hexane, b.p. 119·5° to 120·7°/769 mm corr.

Spectroscopic examination showed that the two products (1) and (2) were identical, that is, that each was *trans*-1 : 3-dimethyl*cyclo*hexane.

Evans,[56] by catalytic hydrogenation of *m*-xylene, obtained a 1 : 3-dimethyl*cyclo*hexane boiling at 121·6° ±1°/760 mm corr and having n_D^{20} 1·4255. This was evidently the *trans* variety.

1 : 3 : 5-*Trimethyl*cyclo*hexane*.

(1) *cis*. *cis*-3 : 5-Dimethyl*cyclo*hexanone (26 g), purified through the semicarbazone (m.p. 201° to 202°), was added to ethereal methyl magnesium iodide (1·5 mol). The carbinol obtained by usual procedure was dehydrated with naphthalene-β-sulphonic acid and the trimethyl*cyclo*hexene (b.p. 142·2° to 144·2°/769 mm) was reduced with hydrogen in glacial acetic acid in presence of platinum oxide. The 1 : 3 : 5-trimethyl*cyclo*hexane obtained had b.p. 139·7° to 140·2°/763·5 mm uncorr and n_D^{20} 1·4280.

(2) *trans*. *trans*-3 : 5-Dimethyl*cyclo*hexanone (38 g), obtained by the oxidation if *trans*-3 : 5-dimethyl*cyclo*hexanol which had been purified through the hydrogen phthalate, was added to ethereal methyl magnesium iodide (1·5 mol). Usual working-up gave trimethyl*cyclo*hexanol, which, on dehydration with naphthalene-β-sulphonic acid, gave 21 g of 1 : 3 : 5-trimethyl*cyclo*hexene, b.p. 142·8° to 143·8°/766 mm. Catalytic reduction (PtO_2–hydrogen–glacial acetic acid) of the latter gave 1 : 3 : 5-trimethyl-*cyclo*hexane, b.p. 140·3° to 140·8°/749 mm uncorr, n_D^{20} 1·4352.

Previous authors have obtained trimethyl*cyclo*hexane by the hydrogenation of mesitylene. Eisenlohr and Gorr [57] gave the following constants :—

cis	b.p. 140·0° to 140·5°/752 mm
trans	138·0° to 139°/760 mm

αβ′-Dimethyladipic acid and 2 : 4-*dimethylcyclopentanone.*

The oxidation of the dimethyl*cyclo*hexanols to dimethyladipic acids was carried out by means of nitric acid, but with this particular material it was found possible to effect certain useful improvements, which are incorporated in the following account :—

200 g of dimethyl*cyclo*hexanol were added gradually to 450 cc of 50 per cent (weight) nitric acid at 55° with *vigorous* stirring, keeping the temperature between 55° and 60° by *intermittent* external cooling. With practice this operation was completed in 60 to 70 min. The mixture was then stirred, and if necessary cooled, until spontaneous cooling started. The yellow liquid was then evaporated in a 1-litre distilling flask at about 50 mm pressure, with occasional addition of concentrated formic acid, until nitrous fumes were no longer in evidence. 20 g of crystallized barium hydroxide were added and the mixture heated gradually in a fusible metal bath. Some water and dimethyl-succinic acid passed over first, and when the bath temperature reached about 320° crude dimethyl*cyclo*pentanone distilled. The total distillate was saturated with anhydrous potassium carbonate, the aqueous layer separated and the ketone dried over anhydrous potassium carbonate. Distillation gave 52 g, b.p. 150° to 160°, that is, a 30 per cent yield calculated on the original 200 g of dimethyl*cyclo*hexanol. The whole operation from dimethyl*cyclo*hexanol to dimethyl*cyclo*pentanone was completed in 8 hr, as against the several days required by existing practice involving use of a larger proportion (640 cc) of nitric acid, and prolonged evaporation of the (continually diluted) aqueous oxidation product.

The use of ammonium vanadate, frequently recommended as a catalyst in such oxidations, was found to complicate the working-up, and in no way to aid the oxidation. In this and similar processes, oxidation of *cyclo*hexanols appears to be largely catalysed by nitrous acid, and the initial addition of nitrous acid (*e.g.*, as produced by the interaction of a little alcohol and nitric acid in a test-tube) is to be preferred to that of vanadate in cases where the hexanol itself is not rapidly attacked by the nitric acid.

Numerous operations as above were carried out using both *cis*- and *trans*-dimethyl*cyclo*hexanol. The dimethyl*cyclo*pentanone formed was converted into the semicarbazone, and the latter submitted to systematic fractional crystallization.

Starting with *cis*-dimethyl*cyclo*hexanol, 329 g of crude semicarbazone were obtained. Fractional crystallization gave 222 g of m.p. 174° to 175°, 15 g of m.p. 164° to 165°, and an inseparable mixture of lower m.p.

Starting with mainly *trans*-dimethyl*cyclo*hexanol, 306 g of crude semicarbazone were obtained. Fractional crystallization gave 242 g m.p. 174° to 175°, 22 g m.p. 157° to 158°, and an inseparable mixture of lower m.p.

The semicarbazones of m.p. 174° to 175° from the two different sources were identical, showing that the main product was an individual dimethyl-*cyclo*pentanone whatever the configuration of the dimethyl*cyclo*hexanol started with.

2 : 4-*Dimethylcyclopentanone.*

The semicarbazone (225 g) of m.p. 174° to 175° was distilled with a mixture of 300 cc of concentrated hydrochloric acid and 300 cc of water. The mixture of water and ketone obtained was saturated with anhydrous potassium carbonate and the separated ketone dried over anhydrous potassium carbonate. The whole of the ketone boiled within the range 152·8° to 153·2°/768 mm corr, the bulk at 152·9°/768 mm corr. Yield, 266 g or 96 per cent of the possible.

From mixtures of semicarbazones obtained from various sources as mentioned above, mixtures of 2 : 4-dimethyl*cyclo*pentanones were similarly prepared.

2 : 4-Dimethyl*cyclo*pentanone was obtained by Zelinsky [58] and by Haller and Cornubert [59] by the action of dilute acid on 1 : 3-dimethyl-*cyclo*pentan-5-one-1-carboxylic acid. Later it was obtained by Wallach [60] by oxidizing 2 : 4-dimethyl*cyclo*pentan-1-ol-1-carboxylic acid with lead dioxide and dilute acid. Wallach found b.p. 152° to 154° for the ketone, the semicarbazone melting at 165° to 166°.

1 : 3-*Dimethylcyclopentane.*

Method 1. The general plan of Chavanne [61] was adopted :—

(*a*) 4-Methyl*cyclo*hexanol was oxidized with nitric acid to β-methyladipic acid, (*b*) the acid was heated with barium hydroxide at 300° to 320°, giving 3-methyl*cyclo*pentanone, (*c*) the ketone was converted by means of methyl magnesium iodide into 1 : 3-methyl*cyclo*pentanol, (*d*) the carbinol was dehydrated with naphthalene-β-sulphonic acid, (*e*) the dimethyl*cyclo*pentene was hydrogenated (hydrogen–platinum oxide–glacial acetic acid). The dimethyl*cyclo*pentene was a mixture, b.p. 94·0° to 95·0°, the 2 : 4-dimethyl*cyclo*pentane, b.p. 90·6°/752 mm corr, n_D^{20} 1·4095. Spectroscopic examination showed it to be the *trans* form. Chavanne [61] gave b.p. 90·6° to 90·8°/760 mm and n_D^{20} 1·4076. Evans,[56] who started with α-methyladipic acid, obtained for 1 : 3-dimethyl*cyclo*pentane the constants : b.p. 90·5°/760 mm corr, and n_D^{20} 1·4096.

Method 2. *From* 2 : 4-*Dimethylcyclopentanone.* (*a*) Using ketone obtained by cyclizing a mixture of αβ′-dimethyladipic acids : 85 g of ketone were reduced in 350 cc of ether over about 200 cc of water by the gradual addition of 135 g of sodium. 72 g of carbinol were obtained, b.p. 158° to 162°. Of this, 65 g were dehydrated with naphthalene-β-sulphonic acid, and the resulting unsaturated hydrocarbon, b.p. 98° to 101° (38 g) reduced with hydrogen–platinum oxide–glacial acetic acid. Small amounts of unsaturated material were removed with sulphuric acid. Final distillation gave : 1·5 cc boiling below 91·2°/773 mm corr, 9·5 cc b.p. 91·2° to 91·4°, n_D^{20} 1·4097, 20 cc b.p. 91·4° to 91·8°, n_D^{20} 1·4098, 5 cc b.p. 91·8° to 92·4°, n_D^{20} 1·4099, and a product boiling up to 95° with n_D^{20} 1·4109.

(*b*) Using stereochemically individual ketone, b.p. 152·9°/768 mm corr, obtained from the semicarbazone of m.p. 174° to 175°. The ketone (75 g) was reduced as under (*a*), the crude carbinol dehydrated with naphthalene-β-sulphonic acid, and the unsaturated hydrocarbon reduced as before. The product, after being freed from unsaturated compounds (sulphuric acid), was distilled. 0·5 cc boiled below 90·8°/771 mm corr, 1·0 cc had

b.p. 90·8° to 91·0°, n_D^{20} 1·4091, 23 cc had b.p. 91·0° to 91·4°, n_D^{20} 1·4092, and the remainder (5 cc) had b.p. 91·4° to 92·3°, n_D^{20} 1·4093 to 1·4094.

Method 3. Pure dimethyl*cyclo*pentanone, from the semicarbazone, was reduced by Clemmensen's method. The 1 : 3-dimethyl*cyclo*pentane obtained had b.p. 91·2° to 92·2°/759 mm uncorr and n_D^{20} 1·4095.

1 : 2 : 4-*Trimethyl*cyclo*pentane*.

Zelinsky [62] obtained the hydrocarbon by reducing 1 : 2 : 4-trimethyl*cyclo*pentanol, obtained from 2 : 4-dimethyl*cyclo*pentanone and methyl magnesium iodide. For the hydrocarbon he gave the constants : b.p. 112·5° to 113° corr and n_D^{20} 1·4156.

The methods adopted in the present work were : (*a*) 2 : 4-dimethyl*cyclo*pentanone to 1 : 2 : 4-trimethyl*cyclo*pentanol to 1-chloro-1 : 2 : 4-trimethyl*cyclo*pentane to the Grignard reagent to the hydrogen and (*b*) 1 : 2 : 4-trimethyl*cyclo*pentanol to 1 : 2 : 4-trimethyl*cyclo*pentenes to the saturated hydrocarbon.

Method (a) (1) 128 g of 2 : 4-dimethyl*cyclo*pentanone from mixed dimethyl*cyclo*hexanols were added to 1·5 mol of ethereal methyl magnesium iodide. The carbinol, isolated in the usual way, was not distilled but was dehydrated with naphthalene-β-sulphonic acid. 95 g of unsaturated hydrocarbon were obtained, b.p. 115·0° to 120·5°/764 mm, and this on reduction with hydrogen–platinum oxide–glacial acetic acid gave a partly unsaturated product which was freed from unsaturation by being shaken with several successive small quantities of concentrated sulphuric acid. Washing, drying, etc., gave 1 : 2 : 4-trimethyl*cyclo*pentane, b.p. 113·0° to 117·2°/753 mm.

(2) 42 g of 2 : 4-dimethyl*cyclo*pentanone from mixed dimethyl*cyclo*hexanols were similarly converted into 1 : 2 : 4-trimethyl*cyclo*pentanol, which, without purification, was dehydrated by heating with iodine. The trimethyl*cyclo*pentene formed had b.p. 116° to 118° (mainly 117·2° to 117·8°) at 762 mm, and when reduced (hydrogen–platinum oxide–acetic acid) gave 1 : 2 : 4-trimethyl*cyclo*pentane, b.p. 113·5° to 114·3°/752 mm.

(3) 61 g of 2 : 4-dimethyl*cyclo*pentanone, from the semicarbazone, m.p. 174° to 175°, were similarly converted into 1 : 2 : 4-trimethyl*cyclo*pentanol, which (62 g) was dehydrated with naphthalene-β-sulphonic acid, the product then being reduced as above. After removal of unsaturated material with sulphuric acid, 1 : 2 : 4-trimethyl*cyclo*pentane was obtained, b.p. 113·5° to 117·5°/774·5 mm. The value of n_D^{20} increased from 1·4156 for the fraction 113·5° to 114·0° to 1·4179 for the highest 0·5 fraction.

Method (b) (1) 42 g of 2 : 4-dimethyl*cyclo*pentanone, from *cis*-dimethyl*cyclo*hexanol, was similarly converted into 1 : 2 : 4-trimethyl*cyclo*pentanol (43 g). The latter, without being distilled, was shaken repeatedly with concentrated hydrochloric acid, and the chloride obtained dried over sodium sulphate. 32 g were obtained, b.p. 35° to 39°/20 mm.

The chloride was converted into the Grignard reagent by heating in ethereal solution with an excess of magnesium previously activated with ethyl bromide. Treatment of the Grignard reagent with ice and dilute acid gave a partly unsaturated product, which was submitted to catalytic hydrogenation (hydrogen–platinum oxide–acetic acid). Fractionation of the saturated hydrocarbon gave 1 : 2 : 4-trimethyl*cyclo*pentane, b.p. 115·0° to 116·5°/771 mm.

(2) 112 g of 2 : 4-dimethyl*cyclo*pentanone, from the semicarbazone, m.p. 174° to 175°, was converted by methyl magnesium iodide into the trimethylcarbinol, b.p. 61° to 62°/14 mm (107 g). Concentrated hydrochloric acid converted the latter into 1 : 2 : 4-trimethyl*cyclo*pentyl chloride, b.p. 35° to 39°/20 mm (74 g), and this was heated in ethereal solution with excess of magnesium which had previously been activated with ethyl bromide. Decomposition with ice and dilute acid, followed by separation, drying, and extraction of traces of unsaturated product (sulphuric acid) gave 1 : 2 : 4-trimethyl*cyclo*pentane (76 g), b.p. 113·5° to 116·5°/769 mm corr. The value of n_D^{20} rose from 1·4151 to 1·4172 from the lowest to the highest 0·5 fraction.

Precision fractionation. The products from all five syntheses of 1 : 2 : 4-trimethyl*cyclo*pentane were mixed and sent to Imperial Chemical Industries Ltd., who carried out a precision fractionation. This clearly indicated the presence of two main components :—

(*a*) b.p. 109·1° to 109·4°	n_D^{20} 1·4109
(*b*) b.p. 116·2°	n_D^{20} 1·4185

It seems probable that the lower boiling isomeride is that in which the 1 and 2 methyls are *trans*, the higher boiling one being that with the 1 and 2 methyls *cis*, and the 4 methyl *trans*. The missing wholly *cis* isomeride probably has a considerably higher b.p.

*Ethyl*cyclo*pentane.*

Purified *cyclo*hexanol was oxidized in the usual manner to adipic acid, and the latter was converted into *cyclo*pentanone by heating it with a little barium hydroxide. The ketone, after being fractionated, was allowed to react with ethyl magnesium bromide.[63] The *cyclo*pentanol underwent dehydration when distilled at the ordinary pressure, giving ethyl*cyclo*pentene, b.p. 109°. Hydrogenation of the ethyl*cyclo*pentene (glacial acetic acid–platinum oxide) gave ethyl*cyclo*pentane, b.p. 102° to 103°/750 mm corr, n_D^{20} 1·4203.

Chavanne and Becker gave b.p. 103·0° to 103·2°/760 mm, $n_D^{19\cdot1}$ 1·4201. Evans [56] gave b.p. 103° ±0·5° and n_D^{20} 1·4201, whilst Pines and Ipatieff [64] found b.p. 103·6°/760 mm, n_D^{20} 1·4196.

1 : 1 : 2-*Trimethyl*cyclo*pentane.*

*iso*Lauronolic acid was prepared by the method of Lees and Perkin [65] and was decarboxylated according to the directions of Crossley and Renouf.[66] The *iso*laurolene obtained was hydrogenated in glacial acetic acid in presence of platinum oxide, and gave 1 : 1 : 2-trimethyl*cyclo*pentane, b.p. 113·6° to 113·8°/753 mm corr, n_D^{20} 1·4232.

1 : 1 : 3-*Trimethyl*cyclo*pentane.*

Pure 4-methyl*cyclo*hexanol was oxidized in the usual manner to β-methyladipic acid and the latter heated with a little barium hydroxide. The 3-methyl*cyclo*pentanone formed was fractionated and allowed to react with methyl magnesium bromide (compare Chavanne [61]). The 1 : 3-dimethyl*cyclo*pentanol obtained had b.p. 54°/10 mm 89 per cent yield. It was converted into 1-chloro-1 : 3-dimethyl*cyclo*pentane by treatment with

concentrated hydrochloric acid and calcium chloride. The chloro-compound was formed in 83 per cent yield, b.p. 40° to 42°/15 mm.

Zinc dimethyl was added gradually to the chloro-compound. When the vigorous reaction was over and addition was complete, the semi-solid mixture was heated for a few minutes and then treated with water and then with dilute hydrochloric acid. The hydrocarbon layer was separated and dried over calcium chloride. The 1 : 1 : 3-trimethyl*cyclo*pentane obtained after fractionation had b.p. 104·0° to 105·0°/749 mm corr, n_D^{20} 1·4115.

Alternatively, the chloro-compound was added gradually to 2 mol of ethereal methyl magnesium iodide, and the reaction completed by heating under reflux. Usual working-up gave a product which was extracted with sulphuric acid until free from unsaturation. The 1 : 1 : 3-trimethyl-*cyclo*pentane obtained had b.p. 104·0° to 105·0°/749 mm corr, n_D^{20} 1·4115. Zelinsky [67] gave b.p. 115° to 116°/760 mm and n_D^{20} 1·4223.

1 : 2 : 3-*Trimethyl*cyclo*pentane.*

Laurolene (1 : 2 : 3-trimethyl-Δ^1-*cyclo*pentene) was prepared from *d*-camphoric acid by the method of Aschan.[68,69] Compare Crossley and Renouf.[70] The hydrocarbon was hydrogenated in glacial acetic acid in presence of platinum oxide and gave dihydrolaurolene (1 : 2 : 3-trimethyl-*cyclo*pentane), b.p. 117·0° to 119·5°/763 mm corr. Fractionation gave various fractions, that with b.p. 117·0° to 117·5° and n_D^{20} 1·4202 being used for spectrographic examination.

1-*Methyl*-2-*ethyl*cyclo*pentane.*

Purified adipic acid was converted into the ethyl ester, b.p. 130°/14 mm. The latter was cyclized to ethyl *cyclo*pentanone-2-carboxylate (b.p. 130°/30 mm; yield, 68 per cent) by the method of Dobson, Ferns, and Perkin,[71] who recorded b.p. 132°/30 mm. Ethylation of the ester was effected by the method of Chiurdoglu,[72] who gave for ethyl 2-ethyl*cyclo*pentanone-2-carboxylate b.p. 109·4° to 109·6°/11 mm, our product, obtained in 75 per cent yield, having b.p. 127°/21 mm. Conversion of this ester into 2-ethyl*cyclo*pentanone (yield, 80 per cent; b.p. 158° to 159°/754 mm corr) was carried out as described by Vavon and Horeau,[73] who recorded b.p. 158° to 160° and 83 per cent yield. Chiurdoglu, using sulphuric instead of hydrochloric acid for the hydrolysis, found b.p. 159° to 160°/751 mm (yield, 77·6 per cent).

The ketone was converted into the semicarbazone, which, after being crystallized from alcohol and then methyl alcohol, had m.p. 189° to 190° (Chiurdoglu gave m.p. 188° to 188·5°). Hydrolysis of the semicarbazone gave the pure 2-ethyl*cyclo*pentanone, b.p. 158·5° to 159·0°/763·5 mm corr.

The ketone was treated with methyl magnesium iodide, when 1-methyl-2-ethyl*cyclo*pentanol was obtained in 80 per cent yield, b.p. 80° to 90°/25 mm (it is, of course, a mixture of *cis* and *trans* forms). Chiurdoglu, who used methyl magnesium bromide, recorded b.p. 60° to 70°/13 mm.

1-Methyl-2-ethyl*cyclo*pentanol was dehydrated with naphthalene-β-sulphonic acid. The unsaturated hydrocarbon, probably 1-methyl-2-ethyl-Δ^1-*cyclo*pentene, had b.p. 127·2° to 127·7°/765 mm corr. Chiurdoglu, using oxalic acid for the dehydration, found b.p. 127·4° to 127·8°/760 mm.

Hydrogenation of the *cyclo*pentene in glacial acetic acid in presence of platinum oxide gave 1-methyl-2-ethyl*cyclo*pentane, which boiled at 122·0° to 125·2°/765 mm corr. Fractionation with an 8-in Dufton column gave little indication of the separation of two isomerides, and the re-combined fractions were therefore sent to Imperial Chemical Industries, who established the presence of an individual of b.p. 121·30°, n_D^{20} 1·4222, and of another of b.p. 127·70°/760 mm, n_D^{20} 1·4291. The higher boiling isomeride is no doubt the *cis* form.

Chiurdoglu, who performed a careful fractionation of much larger quantities than we were able to prepare, established the presence of two forms of 1-methyl-2-ethyl*cyclo*pentane boiling respectively at 121·40° to 121·75°/760 mm (n_D 1·4220) and 127·70° to 128·02°/760 mm (n_D 1·4291).

1-*Methyl*-3-*ethyl*cyclo*pentane*.

Pure 4-methyl*cyclo*hexanol was oxidized with nitric acid by the method given in *Organic Syntheses, Collected*, Vol. I, p. 18. Contrary to the observation of Vogel,[74] the β-methyladipic acid crystallized from the oxidation mixture, and was formed in 50 per cent yield. The acid was converted into 3-methyl*cyclo*pentanone by heating it with barium hydroxide (*Organic Syntheses, Collected*, Vol. I, p. 192). The yield of ketone was 75 per cent.

Interaction of the ketone with ethyl magnesium bromide (Zelinsky,[75] used the iodide) gave 1-methyl-3-ethyl*cyclo*pentan-3-ol, and dehydration of the latter by means of naphthalene-β-sulphonic acid gave an unsaturated hydrocarbon. The latter, when hydrogenated (glacial acetic acid–platinum oxide) gave 1-methyl-3-ethyl*cyclo*pentane, b.p. 120·5° to 121·0°/765 mm corr, n_D^{20} 1·4190.

Zelinsky [76] gave b.p. 120·5° to 121° for the (+)-form of the hydrocarbon.

*Phenyl*cyclo*pentane*.

Pure *cyclo*pentanone was treated with phenyl magnesium bromide, and the resulting 1-phenyl*cyclo*pentanol dehydrated with formic acid.[77] The phenyl*cyclo*pentene was hydrogenated using platinum oxide in glacial acetic acid. The resulting 1-phenyl*cyclo*pentane had b.p. 216·5° to 217·5°/778 mm uncorr, n_D^{20} 1·5252.

Nametkin and Pokrovskaya [78] gave b.p. 215° to 216°/750 mm and n_D^{20} 1·531. Ipatieff and Schmerling [79] found b.p. 219°/760 mm, n_D^{20} 1·5290.

1 : 1-*Dimethyl*cyclo*hexane*.

2 : 2-Dimethyl*cyclo*hexanone was prepared from 2-methyl*cyclo*hexanone as described by Haller and Cornubert.[80] It gave a semicarbazone, m.p. 196° to 197°, from which the regenerated ketone was obtained. Reduction of the latter by Clemmensen's method gave 1 : 1-dimethyl*cyclo*hexane, b.p. 119·2° to 119·7°/757 mm corr, n_D^{20} 1·4290.

Chavanne, Miller, and Cornet [81] found b.p. 119·5° to 120°/751 mm for 1 : 1-dimethyl*cyclo*hexane prepared from 1 : 1-dimethyl*cyclo*hexan-3-ol by dehydration followed by hydrogenation.

1-*Methyl*-3-*ethyl*cyclo*hexane*.

Pure 1-methyl-3-ethylbenzene was hydrogenated in glacial acetic acid in presence of platinum oxide. The product had b.p. 148·9° to 150·9°/759

mm corr, n_D^{20} 1·4340. Signaigo and Cramer,[82] who derived the hydrocarbon from 3-methyl-1-ethyl*cyclo*hexanol (dehydration, hydrogenation), found b.p. 148·4° to 150·0° and n_D^{20} 1·4344.

n-*Butyl*cyclo*hexane*.

*cyclo*Hexanone, previously fractionated, was allowed to react with *n*-butyl magnesium bromide.[82] The butyl*cyclo*hexanol obtained was dehydrated with naphthalene-β-sulphonic acid and the unsaturated hydrocarbon hydrogenated in glacial acetic acid in presence of platinum oxide. The *n*-butyl*cyclo*hexane had b.p. 178·8° to 179·2°/761 mm uncorr, n_D^{20} 1·4416.

Signaigo and Cramer found b.p. 180·1° to 181·2°/760 mm corr and n_D^{20} 1·4408. Evans [56] gave b.p. 180·5° ±0·5° corr and n_D^{20} 1·4410.

cyclo*Heptane*.

*cyclo*Heptanone was prepared by the method of Mosettig and Burger,[83] that is, by the action of diazomethane on *cyclo*hexanone. The yield of *cyclo*heptanone, b.p. 77° to 80°/27 mm was 38 per cent, purified through the semicarbazone, m.p. 163° to 164·5°. Reduction as Willstätter [86] gave *cyclo*heptanol, which was dehydrated with naphthalene-β-sulphonic acid. The *cyclo*heptene was hydrogenated in glacial acetic acid in presence of platinum oxide (compare Vogel [87]). Fractionation gave *cyclo*heptane, b.p. 118·0° to 118·6°/750 mm corr, n_D^{20} 1·4447.

Vogel found b.p. 117·5° to 118°/758 mm and n_D^{20} 1·44355; Ruzicka and Seidel [84] found b.p. 116° to 118°/730 mm. Willstätter and Kametaka [85] recorded b.p. 116·4° to 116·8°/726 mm, 118° corr.

*Phenyl*cyclo*hexane*.

The method of *Organic Syntheses* (1939, **19**, 36) was used. The fractionated product had b.p. 240·2° to 240·3°/763 mm uncorr, n_D^{20} 1·5264.

Tsukervanik and Siderova [88] found b.p. 232° to 235°/715 mm and n_D^{20} 1·5237.

Tetrahydronaphthalene.

Naphthalene was reduced with sodium and alcohol.[89] The 1 : 4-dihydronaphthalene obtained, after fractionation, was hydrogenated in glacial acetic acid in presence of platinum oxide. The tetrahydronaphthalene obtained had b.p. 207·4° to 208·2°/772 mm uncorr, n_D^{20} 1·5445.

Evans [90] found b.p. 206·8°, n_D^{20} 1·5438.

Hydrindene.

Pure commercial indene was fractionated. The fraction which had b.p. 183·3°/766 mm uncorr and f.p. −1·9° corr was reduced with sodium and alcohol.[91] The crude hydrocarbon was distilled under reduced pressure, then shaken repeatedly with small quantities of concentrated sulphuric acid until no further change occurred, and then distilled in steam, etc. The hydrindene obtained had b.p. 178·9° to 179·1°/773 mm uncorr, n_D^{20} 1·5389.

Evans [90] found b.p. 177·5° to 178·5° and n_D^{20} 1·5383.

1-*Methylhydrindene.*

β-Phenylpropionyl chloride, b.p. 130°/20 mm, was obtained in 96 per cent yield from the acid, by the method of Ingold and Thorpe,[92] who give b.p. 121° to 122°/22·5 mm.

The chloride was converted into α-hydrindone (yield, 65·5 per cent; m.p. 42° to 43°) by the method of Ingold and Thorpe.[92] When α-hydrindone was caused to react with methyl magnesium iodide,[93] a product was obtained which tended to undergo dehydration when distilled. Dehydration was speeded up by the addition of naphthalene-β-sulphonic acid, but was accompanied by marked polymerization (compare Plattner and Wyss,[93] who recorded a 90 per cent dehydration; see also Ruzicka and Peyer).[94]

The 1-methylindene, b.p. 204° to 205°/759 mm uncorr, was hydrogenated in glacial acetic acid in presence of platinum oxide. After nine distillations from sodium, two best fractions were selected with b.p. 186·2° to 186·6°/759 mm uncorr, n_D^{20} 1·5266, and 186·6° to 187·1°/759 mm uncorr, n_D^{20} 1·5261.

Nenitzescu and Ciorianescu [95] for 1-methylhydrindene prepared by a different method, found b.p. 186° to 187° and n_D^{20} 1·52742. Plattner and Wyss,[93] using different methods for the last stage from 1-methylindene, found n_D^{20} 1·5260 and 1·5204. Ruzicka and Peyer,[94] using nickel as hydrogenating catalyst, found n_D^{20} 1·5222.

2-*Methylhydrindene.*

Indene, previously fractionated (see under hydrindene), was converted into 2-bromo-1-hydroxyhydrindene essentially by the method of Pope and Read.[96] It was found that the addition of a dispersing agent materially accelerated the addition of hypobromous acid. The bromo compound was converted into β-hydrindone by the method of Walters.[97] By means of methyl magnesium iodide the hydrindone was converted into 2-hydroxy-2-methylhydrindene,[98] and the latter compound was dehydrated with naphthalene-β-sulphonic acid (compare Ruzicka and Peyer [94]). Hydrogenation of the 2-methylindene in ether in presence of platinum oxide gave 2-methylhydrindene, b.p. 186·1° to 186·3°/758 mm uncorr, n_D^{20} 1·5220.

Kishner [99] found b.p. 183° to 185°/747 mm and n_D^{20} 1·5070.

5-*Methylhydrindene.*

(*a*) Hydrindene. Pure commercial indene was fractionated and then hydrogenated in ethereal solution in presence of platinum oxide. 50 g of indene gave 45 g of hydrindene, b.p. 176° to 178°.

(*b*) 5-Chloromethylhydrindene. Prepared using hydrochloric acid and formalin solution, Arnold [100] gave a product, b.p. 125°/14 mm. Arnold found b.p. 110° to 112°/4 mm, and Plattner and Roniger,[101] b.p. 125°/11 mm. The orientation of the product was not established by Arnold and was therefore checked as follows :—

(1) The chloromethylhydrindene (2 g) was mixed with 30 cc of water, 2 g of potassium carbonate added, and the whole boiled under reflux for 2 hr. The solid separating on cooling was crystallized from light petroleum (b.p. 60° to 80°) and then had m.p. 73° to 74°.

(2) Hydrindene-5-aldehyde was prepared by the method of Gattermann [91] as modified for *p*-tolualdehyde in *Organic Syntheses*, Vol.

XII, p. 80. The product, b.p. 250° to 260°, was reduced with hydrogen in alcoholic solution in presence of platinum oxide and a few drops of aqueous ferric chloride solution (compare Carothers and Adams [102]). The resulting carbinol was distilled (b.p. 264° to 266°) and then crystallized from light petroleum (b.p. 60° to 80°), when it had m.p. 73° to 74° (Found: C, 81·04; H, 8·14. $C_{10}H_{12}O$ requires C, 81·02; H, 8·16 per cent). A mixture of the two carbinols from the different sources melted at 73° to 74°.

(*c*) 5-Methylhydrindene. 65 g of 5-chloromethylhydrindene were converted into the Grignard reagent in presence of 12 g of magnesium, completing the interaction by heating for 1 hr under reflux. Decomposition with ice and dilute acid, followed by extraction and drying over calcium chloride and distillation from sodium gave 21 g of 5-methylhydrindene. This, on fractionation, gave best fractions having (*a*) b.p. 201·6° to 202·2°/773·5 mm uncorr, n_D^{20} 1·5321 and (*b*) b.p. 202·2° to 203·2°/773·5 mm uncorr, n_D^{20} 1·5324.

Plattner and Roniger gave n_D^{20} 1·5332.

2-Ethylhydrindene.

β-Hydrindone, prepared as described under 2-methylhydrindene was treated with ethyl magnesium bromide (2 mol). The 2-hydroxy-2-ethylhydrindene was obtained in 62 per cent yield and was dehydrated with naphthalene-β-sulphonic acid. Considerable polymerization occurred. The 2-ethylindene had b.p. up to 220° and on hydrogenation (glacial acetic acid-platinum oxide) gave 2-ethylhydrindene, b.p. 213° to 214°/767 mm corr, n_D^{20} 1·5176. Ruzicka and Peyer [94] recorded no corresponding constants for their hydrocarbon, which they prepared by the above method.

2 : 5-Dimethylhydrindene.

A mixture of 50 g of 2-methylhydrindene (prepared as above), 75 g of 40 per cent formaldehyde solution, and 250 cc of concentrated hydrochloric acid was stirred at 60° to 70° for 14 hr, hydrogen chloride being passed through continuously. The cooled mixture was separated, and the aqueous layer extracted with benzene. The dried (calcium chloride) benzene extract, which had been mixed with the first oil layer, was fractionated, when 38 g of 2-methyl-5-chloromethylhydrindene were obtained, b.p. 138° to 140°/12 mm.

The chloromethyl compound (38 g) was gradually added to 7 g of magnesium in dry ether. A little magnesium previously activated with ether and ethyl bromide was added to start interaction, and when this had subsided the mixture was heated under reflux for 2 hr. Ice and dilute acid were added to the cooled mixture, the ether layer was separated, and the dried ether solution distilled under reduced pressure. The fraction, b.p. 80° to 95°/12 mm, was fractionated and gave 2 : 5-dimethylhydrindene, b.p. 207° to 209°/767 mm corr, n_D^{20} 1·5200.

Toluene.

Pure commercial toluene-*p*-sulphonamide was crystallized twice from methyl alcohol. The m.p. was 138° to 139°. It was mixed with phosphoric

acid and distilled in superheated steam. The toluene formed was distilled repeatedly over sodium, and finally had b.p. 110·6° to 110·8°/762·5 mm corr, and n_D^{20} 1·4971.

Timmermans and Martin [103] recorded b.p. 110·80° and n_D^{20} 1·49685.

p-Xylene.

Three methods of preparation were examined :—

(1) *p*-Dibromobenzene and methyl iodide were treated with sodium.[106]

(2) *p*-Tolyl magnesium bromide was treated with methyl sulphate.[107]

(3) *p*-Iodotoluene and methyl iodide were treated with sodium.

No one of these methods was promising, and the combined products were boiled under reflux with sodium until no further change occurred. The distilled hydrocarbon (b.p. 132° to 141°) was shaken with 5 per cent oleum until in solution and water then added until a stiff paste resulted. The crystalline solid sulphonic acid was filtered, dissolved in the minimum water, and the solution boiled until free from oil or smell. The sulphonic acid was filtered from the cooled mixture and distilled in superheated steam in presence of phosphoric acid. The xylene formed was dried and fractionated from sodium. It had b.p. 139·2° to 139·4°/763 mm uncorr and f.p. 13·2° corr, n_D^{20} 1·4966. Richards, Stull, Mathews, and Speyers [104] gave b.p. 136·2° to 136·4°/764 mm corr and f.p. 13·1° to 13·2°. Timmermans and Martin [105] found b.p. 138·4°/760 mm and f.p. 13·35°.

Hemimellitene (1 : 2 : 3-*Trimethylbenzene*).

Commercial pure 4-*m*-xylidine was converted into the formyl derivative, which was crystallized to constant m.p. 166° to 167°. Hydrolysis, followed by a diazo-reaction, gave 4-iodo-*m*-xylene. The Grignard reagent from the latter reacted vigorously with methyl sulphate. The product was worked-up on normal lines and gave hemimellitene, b.p. 174° to 176°/758 mm uncorr, n_D^{20} 1·5128.

Auwers,[108] who prepared the hydrocarbon by a Fittig reaction, found b.p. 175·5°/744 mm, $n_D^{19·55}$ 1·513. Mair [109] gives b.p. 176·1°.

Mesitylene (1 : 3 : 5-*Trimethylbenzene*).

Pure 2-bromomesitylene, f.p. +0·8° corr, was converted into the Grignard reagent, which was treated with ice and dilute acid. Fractionation of the hydrocarbon–ether layer gave mesitylene, b.p. 165·8° to 166·0°/761 mm corr, n_D^{20} 1·4991.

Mair [109] records b.p. 164·6° and n_D^{20} 1·4991.

pseudo*Cumene* (1 : 2 : 4-*Trimethylbenzene*).

The method of von Braun and Nelles [110] was used, and gave a product b.p. 168·7° to 171·6°/764 mm corr, n_D^{20} 1·5051. Smith and Cass [111] found n_D^{20} 1·5048, while Mair [109] records b.p. 169·18°.

1-*Methyl-2-ethylbenzene.*

The Fittig reaction between *o*-iodotoluene, methyl iodide, and sodium gave a hydrocarbon, b.p. 163·5° to 164·5°/760 mm corr, n_D^{20} 1·5040.

Auwers,[108] using the same method, found b.p. 164° to 165° and n_D^{20} 1·504.

1-*Methyl*-3-*ethylbenzene*.

Pure *m*-toluidine was converted into *m*-tolunitrile by the diazo-method. Interaction of the nitrile with 2 mol of methyl magnesium iodide gave a 65 per cent yield of *m*-methylacetophenone, b.p. 110°/16 mm. Clemmensen reduction of this ketone [108] gave 1-methyl-3-ethylbenzene, b.p. 160·5° to 162·5°/759 mm corr. Auwers found b.p. 161·5° to 162·5°.

1-*Methyl*-4-*ethylbenzene*.

This compound was prepared by the Clemmensen reduction of pure *p*-methylacetophenone. It had b.p. 160·5°/747 mm corr and n_D^{20} 1·4959.

Auwers,[108] who used the same method, gave b.p. 161° to 162° and n_D^{20} 1·496.

n-*Propylbenzene*.

The most obvious method for the synthesis of this hydrocarbon was to reduce propiophenone by Clemmensen's method, but this proved unsatisfactory, the product containing unsaturated material, a fact suggesting that isomerization might also be suspected.

γ-Phenylpropyl alcohol, obtained in a very pure state by the Bouveault reduction of ethyl β-phenylpropionate, was converted into the bromide by means of phosphorus tribromide. The bromide, b.p. 106° to 107°/10 mm, was allowed to react with excess of magnesium in ether, the reaction being completed by boiling under reflux. Normal working up after treatment with water and dilute acid gave a mixture of *n*-propylbenzene, allylbenzene, and diphenylhexane. This was hydrogenated in glacial acetic acid (platinum oxide) and then fractionated. The *n*-propylbenzene had b.p. 160·5° to 161·3°/760 mm corr, n_D^{20} 1·4921.

Auwers [108] gave b.p. 158° to 159° and n_D^{20} 1·492.

m-*Cymene* (1-*Methyl*-3-iso*propylbenzene*).

Commercial pure *m*-toluic acid was converted into the acid chloride, b.p. 92° to 93°/9 mm, and thence into the amide, which after crystallization from benzene and from carbon tetrachloride melted at 95° to 96°. The acid obtained by hydrolysis of the amide was converted into the methyl ester, and the latter treated with methyl magnesium iodide.[108] The resulting carbinol was dehydrated with boiling acetic anhydride, and the unsaturated hydrocarbon reduced with sodium and alcohol (Auwers). The *m*-cymene obtained had b.p. 172°/752 mm, n_D^{20} 1·4935.

Richter and Wolff [112] found b.p. 175·6° to 175·8° and n_D^{20} 1·4920.

n-*Butylbenzene*.

To small slices of sodium, covered with 150 cc of pure ether, was added a mixture of 176 g of pure bromobenzene and 176 g of *n*-butyl bromide, addition being adjusted so as to keep the steady reaction going. Normal working-up of the finished reaction gave *n*-butylbenzene, b.p. 184·8° to 185·2°/782 mm uncorr, n_D^{20} 1·4901.

Evans [90] found b.p. 182·1° to 183·1°, n_D^{20} 1·4880.

*iso*Butylbenzene.

Owing to the uncertainty in the literature as to the physical properties of this hydrocarbon, it was prepared by six different methods :—

Method 1. Addition of benzaldehyde (1 mol) to 1·1 mol of ethereal *iso*propyl magnesium bromide gave a 20 per cent yield of phenyl*iso*propylcarbinol. When 3 mol of the Grignard reagent were used, the yield of carbinol became 92 per cent, b.p. 108° to 114°/16 mm. The carbinol was similarly prepared by Grignard,[112a] who found b.p. 112° to 113°/15 mm. The carbinol was converted into the corresponding bromide by the action of phosphorus tribromide (2/3 mol), starting at 0° and finishing at 100°. The bromide, b.p. 117° to 118°/15 mm, was obtained in 55 per cent yield. The bromide was allowed to react with excess of magnesium in ether, the process being completed by boiling under reflux for 30 min. The mixture was cooled, treated with ice and dilute acid, and the whole filtered to remove the solid which had separated. The dried ether solution was distilled and gave 10 cc b.p. 160° to 175°. The distillation residue became solid on cooling. It was mixed with the first solid and crystallized from alcohol, in which it was sparingly soluble, even in the warm. Analysis showed it to be αβ-diphenyl-αβ-di-*iso*propylethane (Found : C, 90·6; H, 9·7. $C_{20}H_{26}$ requires C, 90·2; H, 9·8 per cent).

The distillate (10 cc) was slightly unsaturated and was hydrogenated (glacial acetic acid–platinum oxide). The fractionated hydrocarbon resulting had b.p. 171° to 172°/760 mm uncorr.

Method 2. Pure commercial *iso*butyric acid was fractionated and converted into the chloride by the method of Smith and Lewcock.[113] The chloride (1 mol) was condensed with excess of benzene in presence of 1 mol of aluminium chloride, and gave a 51 per cent yield of *iso*butyrophenone, b.p. 218°/765 mm.[114]

Clemmensen reduction of the ketone gave a hydrocarbon which, after several distillations over sodium, had b.p. 176° to 184°. It contained unsaturated material and was therefore hydrogenated (acetic acid–platinum oxide). It then had b.p. 172° to 180°, mainly 173° to 175°, and further refractionation gave *iso*butylbenzene, b.p. 173° to 174°/782 mm uncorr, n_D^{20} 1·4924.

Method 3. A mixture of 176 g of bromobenzene (1 mol) and 176 g of *iso*butyl bromide (1 mol) was gradually added to 69 g (3 atoms) of sodium in fine slices covered with ether. A steady reaction set in, and was maintained by addition of the bromides. After leaving overnight, the mixture was filtered, and the solid extracted with light petroleum (b.p. 60° to 80°). The combined organic solutions were distilled until the vapour reached 120°, and then steam distilled. Much diphenyl was in evidence. Repeated fractionation over sodium gave about 3 cc of liquid having the approximate b.p. (167° to 169°) of *iso*butylbenzene. It had n_D^{20} 1·4865.

Riess [115] claimed the above as a method for obtaining *iso*butylbenzene. In fact, in our hands, the two bromides appeared to react independently, the main products being diphenyl and di-*iso*butyl, together with unsaturated compounds.

Method 4. Benzyldimethylcarbinol was obtained in 86 to 91 per cent yield, b.p. 96°/10 mm or 110°/17 mm, by the interaction of acetone and 1 mol of benzyl magnesium chloride in ether.[116] The carbinol was

dehydrated by heating it with iodine, several repetitions being necessary. The unsaturated hydrocarbon after being shaken with alkali to remove iodine had b.p. 180° to 182°/750 mm (Grignard [117] dehydrated with acetic anhydride and obtained the unsaturated hydrocarbon with b.p. 183° to 185°/748 mm). It was hydrogenated (acetic acid–platinum oxide) and gave *iso*butylbenzene which, after several distillations from sodium, had b.p. 169° to 170°/760 mm uncorr, n_D^{20} 1·4825.

Repetition of this method led to *iso*butylbenzene with b.p.

(*a*) 171·8° to 172·2°/749 mm uncorr and n_D^{20} 1·4860.
(*b*) 172·2° to 172·4°/749 mm uncorr and n_D^{20} 1·4860.
(*c*) 172·4° to 172·5°/749 mm uncorr and n_D^{20} 1·4863.

Method 5. Benzyldimethylcarbinol was converted into the chloride, b.p. 65°/10 mm, by means of hydrogen chloride, and then heated with pyridine.[118] The unsaturated hydrocarbon had b.p. 180° to 183°/760 mm and after hydrogenation (acetic acid–platinum oxide) gave *iso*butylbenzene, b.p. 172·2° to 172·6°/760 mm uncorr, n_D^{20} 1·4871.

Method 6. Benzyl chloride (1 mol) was added to 1·5 mol of ethereal *iso*propyl magnesium bromide, the mixture subsequently being boiled under reflux for a day. Treatment with ice and dilute acid, and normal working-up gave *iso*butylbenzene with b.p. 169·8° to 170·0°/747 mm uncorr, n_D^{20} 1·4872.

Pure iso*butylbenzene*.

The best material from all the above preparations was combined and sulphonated. The barium sulphonate was crystallized from water and then distilled in superheated steam in presence of phosphoric acid. The pure *iso*butylbenzene had b.p. 172·3°/758 mm corr, n_D^{20} 1·4870.

tert-*Butylbenzene*.

The hydrocarbon was prepared by the method of Verley [119] and fractionated over sodium. It then had b.p. 169°/760 mm uncorr, n_D^{20} 1·4932.

McKenna and Sowa [120] gave b.p. 167·0°.

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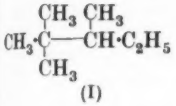
THE SYNTHESIS OF SOME HYDROCARBONS.

By W. J. Hickinbottom and C. R. Porter (with Florence Edwards, Elsa Schlüchterer, and F. Spitzer).

Introduction.

This paper records the preparation of some hydrocarbons carried out in the Departments of Chemistry and Chemical Engineering in the University of Birmingham for a project sponsored by the Ministry of Aircraft Production and later by the Institute of Petroleum.

The programme included the synthesis of the paraffins (I), (II), (III), and (IV), 4-methylindane (V), *iso*durene (VI), and other alkyl benzenes.



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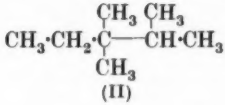

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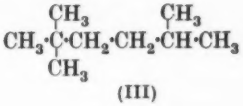

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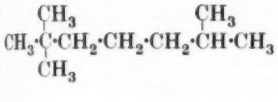
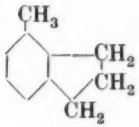
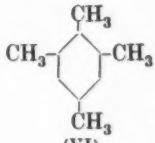


(IV)



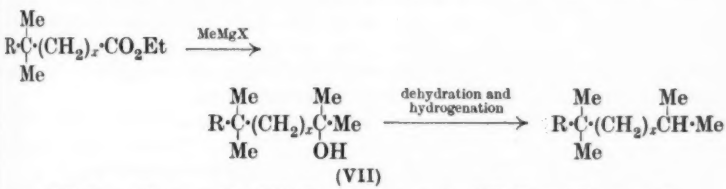
(V)



(VI)

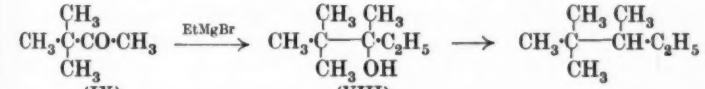
The general plan for the synthesis of the paraffins (I)–(IV) was to use the reaction of a suitable alkyl magnesium halide with an ester or ketone to give an alcohol, which by dehydration and hydrogenation of the resulting olefin gave the required paraffin.

The following schemes illustrate the stages in these preparations :—



(VII)

[II, R = Et, $x = 0$; III, R = Me, $x = 2$; IV, R = Me, $x = 3$]



(IX) (VIII)

It is known that the alcohols of the type (VII) and (VIII) suffer structural rearrangement on dehydration with mineral acids or iodine. Thus (VIII)

is reported to give a mixture of 20 per cent of 2 : 3 : 3-trimethylpentene-4 and 80 per cent of 2 : 2 : 3-trimethylpentene-3 on dehydration with iodine.[1]

It was essential in these syntheses that there should be no isomeric rearrangement on dehydration. Of the two available methods, that depending on the pyrolysis of esters to olefins [2,3] is not generally useful for the dehydration of tertiary alcohols. The Tschugaeff method, making use of the decomposition of the methylxanthate of the alcohol RO·CS·SMe, has the disadvantage of being inconvenient.

It was found that the dehydration of (VIII) could be brought about by refluxing with an excess of acetic anhydride and sodium acetate. The olefin thus formed consisted very largely of 2 : 2 : 3-trimethylpentene-3, and there was no evidence of isomerization of the carbon skeleton during the dehydration.

The same technique was applied in the dehydration of two alcohols (VII) (R = Et, $x = 0$: R = Me, $x = 3$), and in each case there was no isomerization during the dehydration.

It would appear, from a limited number of observations, that this method provides a convenient and easy method of dehydrating tertiary alcohols, without change of configuration. Subsequent work has confirmed these results and has permitted the development of a new method for tertiary alcohols which has considerable advantages over the methylxanthate of Tschugaeff. A full account will be published later.

During the course of this work it was observed that methyl *tert*-butyl ketone (IX) by reaction with ethylmagnesium bromide gave not only the required product (VIII) but also pinacolyl alcohol and an unsaturated ketone subsequently identified as 2 : 2 : 3 : 6 : 6-pentamethylhept-3-ene-5-one (X).[4]

$$\underset{\text{(IX)}}{2CMe_3\cdot CO\cdot CH_3} \longrightarrow \underset{\text{(X)}}{CMe_3\cdot \overset{\overset{CH_3}{|}}{C}\cdot CH\cdot CO\cdot CMe_3}.$$

This substance obviously arises from the self-condensation of the ketone: that the Grignard reagent is responsible for the change is shown by the observation that Grignards, which are known to react sluggishly with a carbonyl group, bring about an increased yield of the condensation product. Thus *tert*-butyl magnesium chloride gives practically none of the normal product; there is formed instead a mixture of the condensation product (X) and the reduction product pinacolyl alcohol.

There are a few recorded observations of the self-condensation of esters under the influence of Grignard compounds,[5] compare Conant and Blatt,[6] but similar observations on ketones appear to be very limited.[7,8]

This is all the more surprising in view of the extensive application of the Grignard reaction to ketones, and the known tendency for high boiling products to be formed.[6] It is now clear from study of the reaction of other ketones to suitable Grignard reagents, that condensation, indeed, occurs to a smaller or greater extent in many Grignard reactions. This observation is strengthened by the subsequent observations of Shine and Turner [9] and of Hey and Morris.[10]

The alkylbenzenes described in this paper were all prepared by reaction of the corresponding halogen compounds with the required alkyl bromides

in dry ether solution under the influence of sodium. Since the products are to be examined for infra-red and ultra-violet absorption spectra these preparations afford the opportunity of deciding if the reaction proceeds by a normal replacement of the halogen or if the alkyl group enters some other position. It might appear from the observations of Morton and his co-workers that the action of sodium on substituted benzenes having one or more methyl groups may lead to smaller or greater substitution in the side chain and the consequent formation of isomeric hydrocarbon.

Report on the Preparation of Pure Hydrocarbons.

(1) 2 : 2-*Dimethylpentane.*

This paraffin was prepared by two different methods :—

(*a*) By reaction of *tert*-butyl magnesium chloride with allyl bromide, and by subsequent hydrogenation of the resulting 4 : 4-dimethylpentene-1.

(*b*) By pyrolysis of the acetate of 4 : 4-dimethylpentanol-2 to a mixture of 4 : 4-dimethylpentene-1 and 2. Hydrogenation in alcohol (PtO_2) gave the required paraffin.

The hydrocarbon had the following constants :—

(*a*) b.p. 78·9° to 79·1°/760 mm (corr), n_D^{21} 1·3824.
(*b*) b.p. 79·0° to 79·2°/760 mm (corr), n_D^{15} 1·3837.

(2) 2 : 2 : 3-*Trimethylpentane.*

tert-Butyl methyl ethyl carbinol (b.p. 47° to 48°/13 mm, n_D^{15} 1·4395) was obtained by the reaction of ethyl magnesium bromide with pinacolin, together with some pinacolyl alcohol and 2 : 2 : 3 : 6 : 6-pentamethylheptene-3-one-5.[4]

tert-Butyl methyl ethyl carbinol was dehydrated without any alteration in carbon skeleton (compare Whitmore and Laughlin [11] and Wibaut *et al.*[12]) by heating the alcohol (65 g) with acetic anhydride (162 g) and fused sodium acetate (65 g) for 48 hr under reflux and then slowly distilling up to 110°. The residue on further heating with more acetic anhydride and fused sodium acetate gave more olefin (total yield 43 g).

After refluxing over sodium, the greater part of the olefin distilled at 110·4° to 110·7°/760 mm (corr), n_D^{17} 1·4224, and was shown by ozonolysis to consist of 2 : 2 : 3-trimethylpentene-3 without any serious amount of the isomeric 2 : 2-dimethyl-3-ethylbutene-3.

Hydrogenation in alcohol (PtO_2) gave the paraffin, b.p. 110·0° to 110·2°/760 mm (corr), n_D^{17} 1·4043.

(3) 2 : 3 : 3-*Trimethylpentane.*

The following scheme was used to prepare this paraffin :—

$$\underset{\text{(XI)}}{C_2H_5CMe_2\cdot CO_2Et} \xrightarrow{MeMgI} \underset{\text{(XII)}}{C_2H_5CMe_2\cdot CMe_2(OH)} \longrightarrow \underset{\text{(XIII)}}{C_2H_5CMe_2\cdot CMe{:}CH_2} \longrightarrow C_2H_5CMe_2\cdot CHMe_2$$

1. Dimethyl ethyl acetic acid was prepared by three different methods :—

(*a*) From *p-tert*-amyl phenyl by oxidation with alkaline permanganate.

(*b*) From 5-*tert*-amyl furoic acid by oxidation with alkaline permanganate.

(*c*) From the amide of dimethyl ethyl acetic acid by hydrolysis or by the action of nitrous acid. This amide was obtained in 80 per cent yield by the action of sodamide on *tert*-amyl phenyl ketone, which in turn had been prepared by the methylation of phenyl *n*-propyl ketone or the ethylation of phenyl *iso*propyl ketone.

Dimethyl ethyl acetic acid used in this preparation melted at −20° to −19° and boiled at 184° to 185° (uncorr); its ethyl ester (I) boiled at 139° to 141°.

2. Reaction of the ester (XI) with a 20 per cent excess of methyl magnesium iodide gave 2 : 3 : 3-trimethylpentanol-2 (XII) in 52 per cent yield. The pure alcohol melts at −8° to −6°, boils at 158·5° to 160° (uncorr), n_D^{19} 1·4387, and is characterized by its 3 : 5-dinitrobenzoate, m.p. 81° to 82°.

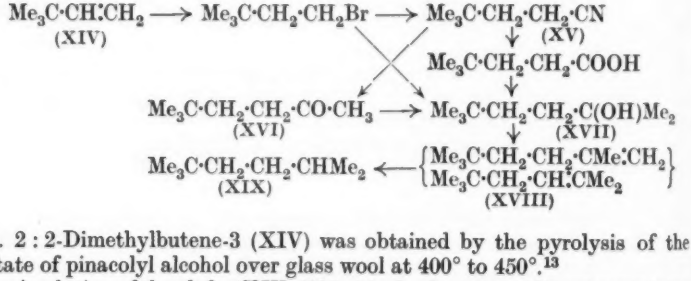
3. Dehydration to the olefin (XIII) was accomplished without any isomerization by heating the alcohol (58 g) for 1 hr with acetic anhydride (100 g) and anhydrous sodium acetate (100 g). The olefin formed during this operation was removed by slow distillation through an efficient column till a temperature of 108° at the still head is reached. The residue was heated with a further quantity of acetic anhydride and the operation repeated till no further olefin was formed.

The yield of crude olefin was 25 g, and after the usual treatment to free it from acetic acid and water, it was distilled over sodium : b.p. 107·7° to 107·9°, n_D^{17} 1·4177.

4. Hydrogenation of the olefin in ethyl alcohol (Pd black) gave 2 : 3 : 3-trimethylpentane, b.p. 117·2° to 117·4°, n_D^{17} 1·4080.

(4) 2 : 2 : 5-*Trimethylhexane.*

The following scheme of synthesis was employed :—



1. 2 : 2-Dimethylbutene-3 (XIV) was obtained by the pyrolysis of the acetate of pinacolyl alcohol over glass wool at 400° to 450°.[13]

2. A solution of the olefin (XIV) (205 g) in dry benzene (2 litres) containing 3 g of ascaridole was slowly run into a 20-litre bottle filled with dry hydrogen bromide. There was a rapid absorption of the gas, and hydrogen bromide was passed into the bottle to maintain the pressure at approximately

atmospheric. After keeping for two or three days, with occasional stirring, the benzene solution was washed, dried, and distilled. 1-Bromo-3 : 3-dimethylbutane was collected at 132° to 136°/760 mm. (Yield 326 g; 81 per cent of theory.)

3. 1-Bromo-3 : 3-dimethylbutane refluxed with a 20 per cent excess of potassium cyanide for 20 hr yielded 1-*cyano*-3 : 3-*dimethylbutane* (XV) (50 per cent yield), b.p. 167·5° to 169·5°. (Found : C, 75·3; H, 11·7; N=12·9. $C_7H_{13}N$ requires C, 75·6; H, 11·8; N, 12·6 per cent.)

4. Hydrolysis of the nitrile (XV) by boiling with twice its weight of potassium hydroxide in five times its weight of alcohol for 20 hr gave 2 : 2-dimethylbutane-1-carboxylic acid, m.p. +3°, b.p. 206° to 208° in almost theoretical yield. (Amide, m.p. 137° to 138°; anilide, m.p. 126° to 128°.)

5. Reaction of the nitrile with methyl magnesium iodide in ethereal solution gave 2 : 2-dimethylhexan-5-one (XVI) in 50 per cent yield, b.p. 154° to 156°—*semicarbazone*, m.p. 177° to 178°. (Found : C, 58·9; H, 10·2. $C_9H_{19}ON_3$ requires C, 58·35; H, 10·35 per cent.)

6. 2 : 2 : 5-Trimethylhexan-5-ol (XVII) was prepared by three different methods, and the identity of the alcohol from each was confirmed by a comparison of the melting point of the pure alcohol and its 3 : 5-dinitrobenzoate. The alcohol obtained from hydrolysis of the dinitrobenzoate boils at 165·5°/748 mm, m.p. 20° to 21°, and has a camphoraceous odour.

The 3 : 5-*dinitrobenzoate*, m.p. 94° to 96°. (Found : C, 57·0; H, 6·6; N, 8·0. $C_{16}H_{22}O_6N_2$ requires C, 56·75; H, 6·55; N, 8·25 per cent.)

Preparation 1.

1-Bromo-3 : 3-dimethylbutane (67 g) in three volumes of dry ether was converted into Grignard compound by reaction with activated magnesium, and to the solution thus obtained 23·5 g of dry acetone diluted with ether were added. The reaction was completed by refluxing for 1 hr. The alcohol isolated from the reaction product was collected at 166·5° to 167·5° and melted at 11°. It was purified by converting it into 3 : 5-dinitrobenzoate and subsequent alkaline hydrolysis of the pure ester. Yield of pure alcohol, m.p. 20° to 21°, 22·5 g.

Preparation 2.

The crude alcohol, m.p. 12°, was obtained in 65 per cent yield by reaction of a 25 per cent excess of methyl magnesium iodide with 2 : 2-dimethylhexanone-5.

Preparation 3.

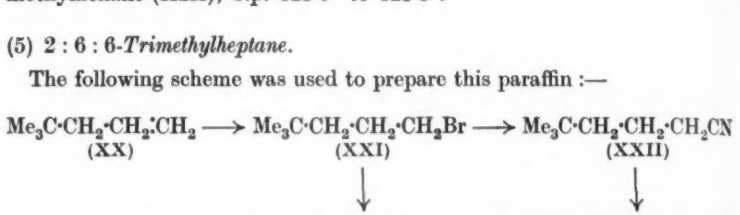
Reaction of the ethyl ester of 3 : 3-dimethylbutane-1-carboxylic acid with an excess of methyl magnesium iodide gave the crude alcohol, m.p. 10° to 12°.

7. The pyrolysis of the acetate of 2 : 2 : 5-trimethylhexanol-5 (b.p. 182° to 183°/748 mm, 83°/28 mm, n_D^{20} 1·4176) at 450° gave the mixture of olefins (XVIII) in 80 per cent yield—b.p. 124·9° to 125·4°/740 mm, n_D^{18} 1·4158. (Found : C, 85·4; H, 14·5. C_9H_{18} requires C, 85·6; H, 14·4 per cent.) Ozonolysis in chloroform gave 5 : 5-dimethylhexanone-2 (XVI) as the main product with small amounts of *tert*-butyl acetic acid.

8. Hydrogenation of the olefin mixture in alcohol (PtO_2) gave 2 : 2 : 5-trimethylhexane (XIX), b.p. 123·0° to 123·5°.

(5) 2 : 6 : 6-*Trimethylheptane.*

The following scheme was used to prepare this paraffin :—



1. 4 : 4-Dimethyl-1-bromopentane (XXI) was obtained by the addition of hydrogen bromide to 4 : 4-dimethylpentene-1 (XX) in presence of a small amount of ascaridole using the technique already described in the preparation of 2 : 5 : 5-trimethylhexane.

The bromide boiled at 55° to 56°/20 mm n_D^{17} 1·4500, and was free from the isomeric 2-bromo compound.

2. The bromide (XXI), on refluxing with alcoholic potassium cyanide, yields 4 : 4-*dimethyl*-1-*cyanopentane* (XXII)—a colourless liquid of camphoraceous odour, b.p. 87°/22 mm. (Found C, 76·6; H, 11·8; N, 11·2. $C_8H_{15}N$ requires C, 76·7; H, 12·1; N, 11·2 per cent.) On hydrolysis, 4 : 4-dimethylpentane-1-carboxylic acid (XXIII) was obtained—white tablets or plates, m.p. 39° to 40°, b.p. 128°/24 mm. (Found : C, 67·1; H, 10·8. Calc : C, 66·7; H, 11·1.) (Whitmore *et al.* gives m.p. 38°.) It was further characterized by its p-*nitrobenzyl* ester, massive tabular crystals from light petroleum (b.p. 40° to 60°), m.p. 52° to 53°. (Found : C, 64·5; H, 7·4. $C_{15}H_{21}O_4N$ requires C, 64·5; H, 7·6 per cent.)

3. The *ethyl ester* of 4 : 4-dimethylpentane-1-carboxylic acid, b.p. 84°/22 mm, 107°/54 mm, n_D^{18} 1·4170 (Found : C, 70·1; H, 11·3. $C_{10}H_{20}O_2$ requires C, 69·9; H, 11·7 per cent), reacts with methyl magnesium iodide to yield 2 : 6 : 6-*trimethylheptan*-2-*ol*, (XXIV) m.p. 42° to 44°, b.p. 87°/22 mm. (Found : C, 75·7; H, 14·1. $C_{10}H_{22}O$ requires C, 75·95; H, 13·9 per cent.) The alcohol is volatile to an appreciable extent, even at room temperature, and has a not unpleasant yet persistent herb-like odour. This alcohol was also prepared by converting (I) into the corresponding Grignard compound and allowing it to react with acetone.

3 : 5-*Dinitrobenzoate*, four-sided plates from light petroleum, m.p. 84°. (Found : C, 58·1; H, 7·0. $C_{17}H_{24}O_6N_2$ requires C, 57·95; H, 6·8 per cent.) The acetate, obtained by refluxing the alcohol with acetic anhydride and sodium acetate, is a liquid with a faint odour, b.p. 93°/20 mm, n_D^{17} 1·4212.

Some decene (VI) is also formed during this preparation. Pyrolysis of the acetate over glass wool at 450° yielded a mixture of decenes (XXV),

b.p. 151° to 152°, n_D^{15} 1·4241. (Found: C, 86·0; H, 14·4. $C_{10}H_{20}$ requires C, 85·6; H, 14·4 per cent.)

Ozonolysis gave 2 : 2-*dimethylheptan-6-one*, b.p. 70° to 71°/17 mm, n_D^{15} 1·4225. (Found: C, 75·5; H, 12·3. $C_9H_{18}O$ requires C, 76·0; H, 12·7 per cent.) Characterized by its 2 : 4-*dinitrophenylhydrazone*, yellow crystals from alcohol, m.p. 107° to 108°. (Found: C, 56·0; H, 6·6. $C_{15}H_{22}N_4O_4$ requires C, 55·9; H, 6·9 per cent.)

4. Hydrogenation of the decene mixture gave 2 : 6 : 6-trimethylheptane, b.p. 148·4° to 148·6°/738 mm, n_D 1·4056.

(6) 3-n-*Butyltoluene*.

3-Bromotoluene (469 g) and *n*-butyl bromide reacted with sliced sodium covered by dry ether to yield 3-*n*-butyltoluene (312 g). It was freed from halogen compounds by prolonged refluxing over sodium, b.p. 204·8°/760 mm (corr), n_D^{20} 1·4912.

3-Bromotoluene was obtained by the diazo reaction from 3-bromo-4-aminotoluene, m.p. 19° to 20°, which had been purified through its acetyl derivative.

(7) 4-n-*Butyltoluene*.

4-*n*-Butyltoluene was prepared by the reaction of 4-bromotoluene and *n*-butyl bromide in ether with sodium.

Fractionation after prolonged heating over sodium gave 4-*n*-butyltoluene, b.p. 206·8°/760 mm (corr), n_D^{20} 1·4904.

p-Bromotoluene was obtained by the diazo reaction from *p*-toluidine, which had been recrystallized twice from light petroleum, and it was purified by fractionation, followed by crystallization to a constant, f.p. 26·2°.

(8) 2-n-*Propyltoluene*.

2-*n*-Propyltoluene was prepared by reaction in ether of *o*-bromotoluene and *n*-propyl bromide with sodium. The hydrocarbon, after refluxing twice for several hours over sodium, was apparently not quite homogeneous. The middle fraction boiled at 184·7°/760 mm, n_D^{20} 1·4990.

o-Bromotoluene was obtained by the diazo reaction from *o*-toluidine, which had been purified by repeated crystallization of its acetyl derivative, b.p. 180·0° to 180·2°/755 mm, n_D^{20} 1·5565.

(9) 4-*Ethyl*-m-*xylene*.

4-Ethyl-*m*-xylene was prepared by reaction in ether of 4-bromo-*m*-xylene and ethyl bromide with sodium, b.p. 188·2°/760 mm, n_D^{20} 1·5035.

4-Bromo-*m*-xylene (b.p. 205·5° to 206·2°/751 mm (uncorr), $n_D^{16\cdot5}$ 1·5527) (420 g) was obtained by the diazo reaction from 4-amino-*m*-xylene (700 g), which had been obtained by the hydrolysis of the pure acetyl derivative, m.p. 129°. The starting material in this preparation was commercial *m*-xylidine, 3 kg of which were purified through the acetate.

(10) 5-*Ethyl*-m-*xylene*.

5-Ethyl-*m*-xylene was prepared by reaction of ethyl bromide and 5-bromo-*m*-xylene in ether with sodium, b.p. 183·6°/760 mm (corr), n_D^{20} 1·4981 to 1·4983.

5-Bromo-*m*-xylene, b.p. 206·9° to 207·0°/743 mm, n_D^{17} 1·5597, was obtained by the deamination of 5-bromo-4-amino-*m*-xylene. This amine, recrystallized separately from light petroleum to constant m.p. 43°, was prepared by the bromination of pure *m*-xylidine in concentrated hydrochloric acid. 700 g of pure *m*-xylidine gave 780 g of pure 5-bromo-4-amino-*m*-xylene.

(11) 2-*Ethyl*-p-*xylene*.

2-Ethyl-*p*-xylene prepared by the Fittig reaction from 2-bromo-*p*-xylene boils at 186·3° to 186·5°/760 mm (corr), n_D^{20} 1·5034 to 1·5040.

2-Bromo-*p*-xylene, m.p. 5·5° to 6·5°, b.p. 205·3°/752 mm (uncorr), $n_D^{15\cdot5}$ 1·5520, was obtained by the diazo reaction from 2-amino-*p*-xylene (m.p. 14·5° to 15·0°, $n_D^{15\cdot5}$ 1·5586) which had been purified through its benzoyl derivative, m.p. 101°.

(12) 2-*Ethylnaphthalene*.

2-Ethylnaphthalene was prepared by the Clemmensen reduction of 2-acetylnaphthalene. The reduction was slow, and the hydrocarbon was purified by conversion into the sulphonic acid, m.p. 75° to 77°, from benzene–chloroform and by subsequent hydrolysis by action of diluted sulphuric acid at 150° to 160°.

2-Ethylnaphthalene boils at 250·4° to 250·6° (uncorr), n_D^{20} 1·5990.

The 2-acetylnaphthalene was obtained in 50 per cent yield by the action of acetyl chloride and aluminium chloride on pure naphthalene in nitrobenzene. It was crystallized to constant m.p. 53·5° to 54·5° from glacial acetic acid.

(13) 1 : 3-*Diethylbenzene*.

1 : 3-Diethylbenzene was obtained in 36 per cent yield by the Fittig reaction from 3-bromoethylbenzene and ethyl bromide, b.p. 180·9°/760 mm (corr), n_D^{20} 1·4953.

3-Bromoethylbenzene, b.p. 201° to 201·5°/750 mm (uncorr), n_D^{20} 1·5454, was prepared by the Clemmensen reduction of 3-bromoacetophenone—412 g of pure bromoethylbenzene being obtained from 770 g of ketone.

m-Bromoacetophenone, m.p. 13·5° to 15°, b.p. 130°/15 mm, obtained by the diazo reaction from 3-aminoacetophenone, m.p. 96° to 97°—785 g of bromo compound from 660 g of amine.

m-Aminoacetophenone was derived by reduction of the corresponding nitro compound with iron and acetic acid, and purified by recrystallization from benzene and alcohol.

(14) 1-*Ethylnaphthalene*.

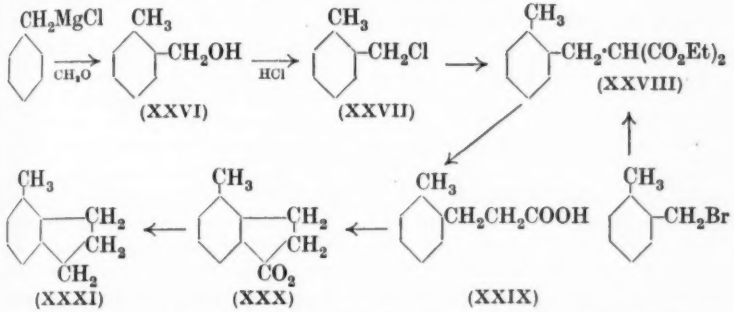
1-Ethylnaphthalene was prepared by two different methods :—

(*a*) the reaction of ethyl bromide with α-naphthalene lithium ;
(*b*) reaction of diethyl sulphate with α-naphthyl magnesium bromide.

The product was refluxed with sodium repeatedly and fractionated. It boils at 250·5° to 251·5°/748 mm (uncorr), n_D^{20} 1·6051.

(15) 4-*Methylindane.*

4-Methylindane was prepared in the following stages :—



o-Methyl benzyl alcohol (XXVI), b.p. 107° to 108°/10 mm, was obtained by reaction of dried trioxymethylene with benzyl magnesium chloride in ether. The purification by crystallization from light petroleum b.p. 40° to 60° to a constant melting point of 35° was achieved only with considerable loss. It yielded *o*-methyl benzyl chloride, b.p. 85° to 86°/17 mm, by reaction in light petroleum with dry hydrogen chloride at 0° over a period of two or three days.

By reaction of *o*-methyl benzyl chloride (XXVII) (91 g) with malonic diethyl ester (110 g) in 250 cc of alcohol containing 15 g of sodium, there was obtained *o*-methyl benzyl malonic diethyl ester (118 g) (XXVIII); 14 g of unchanged malonic ester; 21 g of *di* o-*methyl benzyl malonic* ester, b.p. 235° to 236°/11 mm, m.p. 34° to 35°—massive cube-like crystals from alcohol. (Found : C, 74·7; H, 7·4. $C_{23}H_{28}O_4$ requires C, 75·0; H, 7·7 per cent)—and some *o*-methyl benzyl ethyl ether.

A further amount of *o*-methyl benzyl malonic ester was obtained by reaction of *o*-methyl benzyl bromide with malonic ester.

Hydrolysis of *o*-methyl benzyl malonic ester and decarboxylation of the substituted malonic acid gave β-2-methyl phenyl propionic acid (XXIX), m.p. 102° to 103°.

The acid chloride, b.p. 132° to 133°/16 mm, was obtained in 90 to 95 per cent yield by reaction with thionyl chloride. Cyclization of the acid chloride was brought by aluminium chloride. A solution of the acid chloride (53 g) in 100 cc of light petroleum (b.p. 60° to 80°) was added to 50 g of finely powdered aluminium chloride covered by 30 cc of light petroleum. The reaction mixture was heated gently in a boiling water-bath for 2 hr, then kept for 12 hr, and finally heated for 5 hr under reflux. 4-Methylindan-1-one (XXX) (33 g), m.p. 97° to 98°, was isolated by pouring the reaction mixture into ice-cold dilute hydrochloric acid and steam distilling—2·5 g of unchanged acid were also obtained.

4-Methylindan-1-one was characterized by its *benzylidene* derivative, prismatic needles from ethyl acetate, m.p. 137° to 138°. (Found : C, 87·4; H, 5·8. $C_{17}H_{14}O$ requires C, 87·1; H, 6·0 per cent.)

2 : 4-Dinitrophenylhydrazone—red-brown prisms from pyridine, m.p. 280°.

Clemmensen reduction of the ketone gave 4-methylindane (XXXI), b.p. 203·9°/760 mm, n_D^{20} 1·5358.

(16) 1 : 2 : 3 : 5-*Tetramethylbenzene.*

Reduction of 2 : 4 : 6-trimethyl benzyl chloride by zinc dust in alkaline suspension gave *iso*durene.

2 : 4 : 6-trimethyl benzyl chloride was obtained together with 2 : 4 : 6-trimethyl-1 : 3-dichloromethylbenzene by stirring a mixture of pure mesitylene (50 g), concentrated hydrochloric acid (300 cc), and trioxymethylene (1·6 g) at 70° to 75° for 7 hr, hydrogen chloride being passed in at intervals. After keeping overnight, the upper semi-solid layer was taken up in ether, washed, and distilled. It was resolved by distillation into unchanged mesitylene, 2 : 4 : 6-trimethyl benzyl chloride, b.p. 120° to 130°/17 mm, and a residue which crystallized on cooling—which consisted of 2 : 4 : 6-trimethyl-1 : 3-dichloromethylbenzene—long needles from carbon tetrachloride, m.p. 104° to 105°.

Reduction was effected by heating a stirred mixture of 57 g of the monochloro compound, 100 g of water and 40 g zinc dust to 80°, and then adding over a period of 1 hr a solution of 50 g sodium hydroxide in 100 cc of water. The heating was continued with stirring for 14 hr, and during the last 10 hr 20 g of zinc dust and a solution of 20 g of sodium hydroxide in 50 cc of water were added to complete the reduction.

iso-Durene (22 g) was isolated by steam distillation, b.p. 197·5°, n_D^{20} 1·5130.

(17) *Pentamethylbenzene.*

2 : 4 : 6-Trimethyl-1 : 3-di-chloromethylbenzene was reduced by the method previously described for *iso*durene. 70 g of dichloro compound gave 36 g of pure pentamethyl benzene, b.p. 118° to 118·5°/37 mm—flat needles from alcohol, m.p. 51·5° to 52·5°.

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HYDROCARBON SYNTHESES.

By F. R. Buck, B. B. Elsner, T. Henshall, T. S. Moore, A. R. Murray, S. H. Morrell, G. Müller, M. M. T. Plant, J. C. Smith, and E. R. Wallsgrove.*

Introduction.

This report † completes the series of descriptions of hydrocarbons prepared during the period 1940–43 at Oxford with the support of the Anglo-Iranian Oil Co., Ltd.

In the earlier preparations the aim was to make 2 to 3 litres of each hydrocarbon for engine-tests and for determination of physical constants; later, smaller quantities were asked for in connexion with studies on the infra-red spectra. Many of the preparations involve new syntheses; in others the published methods were modified, either because of unsuitability for large-scale work, or because some of the materials were not available. In most cases alkyl chlorides were used instead of bromides or iodides.

HEPTANES.

By B. B. Elsner, S. H. Morrell, J. C. Smith, and E. R. Wallsgrove.

2-Methylhexane.

I. A small sample (about 100 cc, for spectroscopic work) has been prepared by the interaction of β-methallyl chloride and *n*-propyl magnesium chloride to give 2-methylhexa-1-ene, followed by hydrogenation.

$$\mathrm{Pr{\cdot}MgCl} + \mathrm{ClCH_2{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}{:}CH_2} \longrightarrow \mathrm{Pr{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}{:}CH_2} \xrightarrow{\mathrm{Ni/H_2}} \mathrm{CH_3{\cdot}(CH_2)_3{\cdot}\overset{\displaystyle CH_3}{\overset{|}{C}}H{\cdot}CH_3}$$

To 2 mol of propyl magnesium chloride were added 2 mol of β-methallyl chloride in about 600 cc of dry ether.‡ The solution became milky, and after standing for 2 hr a thick, white precipitate was formed.

To complete the reaction it was necessary to warm the flask and let the reaction mixture stand overnight. Decomposition with ice-water and 20 per cent sulphuric acid was carried out in the normal way.

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* The work was carried out under the general supervision of Dr J. C. Smith in the Dyson Perrins Laboratory, Oxford University. Preparation of the intermediates for 2 : 2 : 3-trimethylpentane and 1 : 3-dimethyl*cyclo*pentane was directed by Professor T. S. Moore at Royal Holloway College, London University.

† A Report (*J. Inst. Petrol.*, 1948, **34**, 339) has dealt with hydrocarbons which were prepared with the aid of zinc dialkyls. This section of the hydrocarbon scheme was supervised by Dr B. B. Elsner.

‡ When the hydrocarbons are required for spectroscopic investigation it is essential that all ether used should be entirely free from benzene.

After evaporation of the ether the olefin was distilled, and then reduced with Raney nickel and hydrogen under a pressure of about 70 atm. The paraffin, washed with water, dried over sodium sulphate, and distilled from sodium, had b.p. 90°, n_D^{20} 1·3851. The yield was about 30 per cent, and there was a considerable amount of higher-boiling hydrocarbon.

B. B. E.

II. The method adopted for preparing a bigger quantity was that first used by Edgar, Calingaert, and Marker,[1] and subsequently by Wibaut, Hoog, Smittenberg *et al.*[2]

$$n\text{-BuMgCl} + CH_3\cdot\overset{CH_3}{\underset{|}{C}}O \longrightarrow CH_3\cdot\overset{CH_3}{\underset{OH}{\overset{|}{C}}}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3 \xrightarrow[+H_2]{-H_2O} CH_3\cdot\overset{CH_3}{\overset{|}{C}}H\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$$

To a solution of *n*-butyl magnesium chloride [prepared from 240 g (10 mol) of magnesium and 1040 cc of *n*-butyl chloride (10 mol) in 2000 cc of anhydrous ether, with the addition of a few drops of bromine as catalyst] was slowly added 687 cc (9·7 mol) of acetone * in an equal volume of anhydrous ether. The reaction vessel was well cooled in ice, and the solution vigorously stirred.

After having stood overnight, the mixture was decomposed, first with ice-water and then with sulphuric acid. The ether layer was separated, washed four times with water, then with an aqueous solution of sulphur dioxide to remove the bromine, then with sodium bicarbonate solution, and finally twice more with water. It was dried with sodium sulphate, and the ether evaporated on a water-bath. The residue was fractionally distilled. In the distillate coming over below 100° were 60 cc of water; this probably arose from dehydration of the carbinol.

Two fractions were collected : (*a*) b.p. 139° to 141°, n_D^{20} 1·4179; (*b*) b.p. 141° to 142°, n_D^{20} 1·4185.

There were 760 cc of the latter fraction, corresponding to a 57 per cent yield, calculated on the acetone.

Dehydration of 2-Methylhexan-2-ol.

This dehydration was carried out by distilling 720 cc of the alcohol with 2 g of iodine. The mixture was refluxed for a while and then distilled at the rate of about one drop in 2 sec : at higher rates of distillation the dehydration was incomplete. An azeotropic mixture of 2-methylhexa-1-ene, 2-methylhexa-2-ene, and water distilled over between 77° and 78°.

The water layer was separated and a little of the olefin mixture dried over sodium sulphate and distilled. It boiled at 92° to 94° and had n_D^{20} 1·4089, which indicated that the dehydration was incomplete. It was redistilled with iodine, the water layer separated, and the olefin mixture refluxed for 3 hr with sodium wire. To ensure complete removal of iodine,

* Acetone was dried thoroughly by allowing it to stand over powdered calcium chloride for a week, then it was distilled through an efficient column. The accepted fraction had b.p. 56°.

the mixture was refluxed for 2 hr with Raney nickel and then fractionally distilled, almost all passing over at 93·5° to 95·0°. This fraction (570 cc, 82 per cent yield) had n_D^{20} 1·4081.

When the mixture of olefines contained no trace of halogen it was hydrogenated with Raney nickel as catalyst under a pressure of 70 atm and a temperature of 80°, finally raised to 130°.

The resulting paraffin was washed four times with water then dried over sodium sulphate. Completeness of reduction was confirmed by the Baeyer test. After careful rectification the paraffin boiled at 90·1°/760 mm (corr) and had n_D^{20} 1·3850; the yield was almost theoretical. Edgar, Calingaert, and Marker [1] give b.p. 90·0°, n_D^{20} 1·3851; Smittenberg *et al.*[3] give 90·10° and 1·38493, respectively. A.P.I. Tables give b.p. 90·05° and n_D^{20} 1·38490.

E. R. W.
B. B. E.

3-Methylhexane.

The method adopted was that first used by de Graef [4] and later by Edgar, Calingaert, and Marker.[1]

$$PrMgCl + CH_3{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\underset{|}{C}}O \longrightarrow CH_3{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{\cdot}Pr \xrightarrow[+H_2]{-H_2O} CH_3{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\underset{|}{C}}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

Preparation of 3-Methylhexan-3-ol.

3-Methylhexan-3-ol was prepared by the interaction of *n*-propyl magnesium chloride and methyl ethyl ketone in ether solution on a 10-mol scale; the methyl ethyl ketone had been dried by standing over powdered calcium chloride for two days and was distilled, the fraction boiling at 79° to 79·5°/747 mm being used in the Grignard reaction.

The reaction was carried out, and the product worked up, in exactly the same manner as for 2-methylhexan-2-ol. The product was distilled under normal pressure, 3-methylhexan-3-ol of b.p. 139° to 140°, n_D^{20} 1·4231, being obtained in an average yield of 64 per cent (calc on the methyl ethyl ketone). de Graef [4] and Edgar [1] used *n*-propyl bromide.

Dehydration of 3-Methylhexan-3-ol.

The carbinol obtained in the first two runs was dehydrated with iodine to give a mixture of 3-methylhexa-2-ene and 3-methylhexa-3-ene by distillation. To 700 cc of carbinol was added 2 g of iodine, and the mixture was heated so that the azeotropic mixture of heptenes and water distilled over slowly at 78°; the water layer was separated. The olefin mixture had the rather high refractive index, n_D^{20} 1·4130. This suggested incomplete dehydration, and the olefin was therefore redistilled with some more iodine. The olefin was dried with anhydrous sodium sulphate, refluxed with sodium wire, and then distilled, the fraction coming over at 96° being collected; this was found to be halogen-free and to have n_D^{20} 1·4118.

Owing to the slowness of dehydration on refluxing with iodine the last

two batches of carbinol were dehyrdated with alumina. The carbinol was passed at the rate of 1 drop per sec through an alumina column heated in an electric furnace at 350°. The olefin was separated from the water, dried over sodium sulphate, refluxed with sodium wire, and then distilled. The mixture of olefins coming over between 87° and 96° had n_D^{20} 1·4118.

Hydrogenation to 3-Methylhexane.

The halogen-free olefin mixture was reduced using Raney nickel and hydrogen at 160° and 80 atm. It was observed that the reduction went at first quickly and then slowed down—as though there were double bonds of very different reducibility. The reduction product was washed three times with water to remove any alcohol introduced with the catalyst and then dried over anhydrous sodium sulphate. It had n_D^{20} 1·3887–1·3889, and the Baeyer test showed complete saturation. Sodium wire was then introduced, and the paraffin was distilled from this.

The crude paraffin began to boil at about 70° and the b.p. rose quickly to 91°/760 mm; a slow rise to 91·6° followed, the b.p. and refractive index remaining almost constant to the finish at 91·6° and n_D^{20} 1·3887. A small residue was left in the flask, and it smelt of the carbinol, 3-methylhexan-3-ol, which apparently had come through unchanged.

The small fraction b.p. 70° to 91° was washed with 85 to 90 per cent sulphuric acid and then with 96 per cent sulphuric acid, both layers remaining colourless after vigorous shaking. After the paraffin layer had been washed with water, alkali, water, and then dried with magnesium sulphate it was put into a flask with sodium and redistilled. Boiling again began at 70° (the first 5 cc had n_D^{20} 1·3880), and the temperature rose to 91°. Ether was therefore absent, and it was possible that one of the low-boiling impurities was *n*-hexane (b.p. 69°, n_D^{20} 1·3751) formed during the preparation of the *n*-propyl magnesium chloride.

Altogether 2600 cc of 3-methylhexane of b.p. 91·6° and n_D^{20} 1·3887 were prepared.

Edgar, Calingaert, and Marker [1] give b.p. 91·8°, n_D^{20} 1·38873. Glasgow [5] gives b.p. 91·96°, n_D^{20} 1·3887. A.P.I. Tables give b.p. 91·95° and n_D^{20} 1·38865.

E. R. W.

3-Ethylpentane.

The method used was that of Edgar, Calingaert, and Marker,[1] and of Brooks, Howard, and Crafton.[6]

$$\mathrm{Et{\cdot}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{\cdot}O{\cdot}Et} \xrightarrow[H_2O]{EtMgCl} \mathrm{Et{\cdot}\overset{\overset{Et}{|}}{\underset{\underset{OH}{|}}{C}}{\cdot}Et} \xrightarrow[+H_2]{-H_2O} \mathrm{Et{\cdot}\overset{\overset{Et}{|}}{CH}{\cdot}Et}$$

Triethyl Carbinol.

240 g of magnesium turnings (10 mol) and 1 litre of ether were placed in a three-necked flask fitted with stirrer and condenser, and 645 g of ethyl chloride (10 mol) were added slowly from a tap funnel. When all the magnesium had been dissolved, 510 g of ethyl propionate (5 mol) in 1200 cc of ether were gradually dropped in while the contents of the flask were kept stirred and cooled to 20° to 30°. An additional 500 cc of ether was

added in order to prevent the reaction mixture from setting solid, but it became very difficult to stir. The mixture was then heated in a warm water-bath for ½ hr, cooled and the resulting thick paste stirred into a mixture of ice and ammonium chloride. The ether layer was separated, and the aqueous layer was once extracted with ether; the combined ethereal extracts were dried with sodium sulphate. After removal of the ether the residual carbinol was first distilled under reduced pressure (b.p. 80° to 90°/90 mm) and finally purified by fractionation at atmospheric pressure, the fraction of b.p. 140° to 142° being retained; it amounted to 300 g (50 per cent yield) and had n_D^{20} 1·4294 (literature value, 1·4293).

In the first preparation of this carbinol 900 g of ester were used; the reaction mixture set solid, and difficulty was experienced in working up the product, some ether and carbinol being lost. The yield, however, was 850 g of carbinol, b.p. 142° to 145°.

3-Ethylpenta-2-ene.

300 g of triethylcarbinol were dehydrated by refluxing for 2 hr with 0·5 per cent of iodine, and the resulting mixture slowly distilled through a 30-cm Dufton (glass) column. The main fraction, consisting of an azeotropic mixture of olefin and water came over at 78° to 81°: it was separated and dried (yield 203 g, 80 per cent). 661 g of this crude 3-ethylpentene were refluxed over sodium wire and then slowly distilled through a 60-cm Dufton column. The main fraction (437 g) passed over at 94·7° to 95·4°/755 mm, n_D^{20} 1·4146, and some polymerization occurred. A liquid and a waxy solid were left in the distilling flask. Redistillation yielded a main fraction of b.p. 94·9° to 95·0°/750 mm and n_D^{20} 1·4146. Church, Whitmore, and McGrew [7] give for 3-ethylpenta-2-ene the values, b.p. 96° to 97°/737 mm and n_D^{20} 1·4142, but most authors record b.p. 95·1° to 95·5°, n_D^{20} 1·4129 to 1·4149.[8]

3-Ethylpentane.

367 g of 3-ethylpenta-2-ene, b.p. 94·7° to 95·4°, were hydrogenated in presence of Raney nickel, using a maximum pressure of 100 atm and temperature of 195°. The crude paraffin was washed three times with water, dried with sodium sulphate, and then refluxed over sodium wire. Distillation through a 60-cm Dufton column gave the following fractions:—

Fraction.	°C/760 mm.	g.	n_D^{20}.
I	91·7 to 93·1	11	1·3929
II	93·1 to 93·3	26	1·3932
(Main) III	93·3 to 93·35	302	1·3934
IV	93·35 to 93·5	42	1·3936

Edgar, Calingaert, and Marker [1] give b.p. 93·2° to 93·5°/760 mm, n_D^{20} 1·39366. Brooks, Howard, and Crafton [6] give b.p. 93·47°/760 mm, n_D^{20} 1·39337. A.P.I. Tables give b.p. 93·468° and n_D^{20} 1·39340.

Dehydration with Alumina.

The alumina used contained sulphate, and the temperature (350° to 400°) was higher than intended. As a result a complex mixture of olefins was produced, but there was no tar formation.

The olefin layer (865 cc) was washed twice with 8 per cent sodium hydroxide (which took out the smell of mercaptans), then with water, and dried with sodium sulphate. Distillation through a 60-cm Dufton column gave the following fractions :—

Fraction.	° C.	cc.	n_D^{20}.
I	63 to 83	17	—
II	83 to 92·2	50	1·4062
III	92·2 to 93·0	90	1·4080
IV	93·0 to 93·6	90	—
V	93·6 to 94·2	140	—
VI	94·2 to 94·6	80	—
VII	94·6 to 94·8	80	—
VIII	94·8 to 95·3	300	1·4110

Fractions II, III, and IV after having stood for 15 min over phosphorus pentoxide were redistilled without change of boiling point. In the literature the value given for the refractive index of 3-ethylpenta-2-ene is n_D^{20} 1·4140, and the b.p. is 95°. Data for other heptenes are :—

	B.p., ° C.	n_D^{20}.
2-Methylhexa-1-ene . . .	91	1·4040
2-Methylhexa-2-ene . . .	94·5	1·4075
3-Methylhexa-1-ene . . .	84·0	1·3970
3-Methylhexa-2-ene . . .	85 to 97	1·41

Reduction.

Fractions IV–VIII were mixed and reduced in presence of Raney nickel (up to 200° and 100 atm). The product, which was free from olefins, was dried over magnesium sulphate, refluxed with sodium wire, and then fractionated with a 90-cm Dufton column.

Fraction	° C.	cc.	n_D^{20}.
I	87 to 91·9	50	1·3889
II	91·9 to 91·9	30	1·3892
III	91·9 to 92·1	40	—
IV	92·1 to 92·2	60	1·3896
V	92·2 to 92·2	50	—
VI	92·2 to 92·3	80	1·3895
VII	92·3 to 92·5	130	1·3895
VIII	92·5 to 93·5	140	1·3897
IX	93·5 to 93·55	50	1·3901
X	93·6 to 93·9	20	1·3908

3-Ethylpentane has b.p. 93·3° and n_D^{20} 1·3934.
3-Methylhexane „ 91·8° „ 1·3887.
2-Methylhexane „ 89·7° „ 1·3851.

Dr H. W. Thompson reported that the infra-red spectrum of Fraction III showed it to be largely a mixture of 3-methylhexane with a little 2-methylhexane; Fraction IX seemed to contain 3-methylhexane and 3-ethylpentane.

Action of Alumina on 3-Ethylpenta-2-ene.

As 3-ethylpentan-3-ol had suffered rearrangement over alumina (containing sulphate) it was of interest to see whether the olefin, 3-ethylpenta-2-ene, was unstable under the same conditions.

50 cc of olefin, b.p. 94·9° to 95·0°/755 mm and n_D^{20} 1·4146 (made by the iodine-dehydration method), were passed through a tube filled with the

same specimen of alumina and kept at 360° to 400°. The product was washed, dried, and then distilled. It yielded the following fractions :—

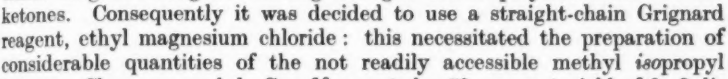
Fraction.	° C.	Per cent.	n_D^{20}.
I	Up to 90	20	1·4034
II	90 to 93	25	1·4050
III	93 to 106	25	1·4101
IV	106 to 120	10	1·4322

Residue—up to 200°.

S. H. M.
J. C. S.

2 : 3-Dimethylpentane.

Attempts to prepare 2 : 3-dimethylpentan-2-ol by the action of *sec*-butyl magnesium chloride on acetone gave only 18 to 25 per cent yields of the rather impure carbinol. Similarly, the action of *iso*propyl magnesium chloride on methyl ethyl ketone gave unsatisfactory results, the branched-chain Grignard reagents having brought about polymerization of the ketones. Consequently it was decided to use a straight-chain Grignard reagent, ethyl magnesium chloride : this necessitated the preparation of considerable quantities of the not readily accessible methyl *iso*propyl ketone. Chavanne and de Graef [9] reported a 50 per cent yield of 2 : 3-dimethylpentan-3-ol from methyl *iso*propyl ketone and ethyl magnesium bromide. We used ethyl chloride and in a preliminary 1-mol run obtained a 47·5 per cent yield ; in a 4-mol run the yield was 66 per cent.



Methyl iso*Propyl Ketone.*

Attempts to prepare the ketone by the action of methyl magnesium chloride on methyl*iso*butyrate or of *iso*propyl magnesium chloride on ethyl acetate gave small yields. It was found that dimethylacetoacetic ester could be hydrolysed with 85 per cent phosphoric acid to methyl *iso*propyl ketone in 50 to 60 per cent yield. But the dimethylation of acetoacetic ester proved to be an expensive process : although dimethyl sulphate could be used for the monomethylation it was an unsatisfactory methylating agent for the second stage. This method of preparing the ketone was therefore abandoned.

*iso*Butyric acid (from Technical Products, Ltd.) was distilled through a 30-cm Dufton column. Only about 10 per cent of the acid had to be rejected, the remainder distilling at 155° to 157°. A mixture of equal volumes of this acid and of glacial acetic acid (1·0 mol *iso*butyric : 1·64 mol acetic) was passed through a Pyrex tube containing pumice covered with thoria and heated to 420°. The tube was of 2·8 cm diameter and the packing (88 cm long) was prepared according to the directions of Herbst and Manske.[10] The acid mixture was delivered by means of a capillary siphon at the rate of one drop every 4 to 6 sec, and a very slow stream of carbon dioxide was passed. At the end of each 24-hr run the product was neutralized with sodium hydroxide solution (20 per cent) : the two layers were

separated, and the aqueous layer extracted twice with pentane (b.p. 32° to 37·5°). The upper layer and the pentane extracts were combined, dried with sodium sulphate, and distilled. Methyl *iso*propyl ketone (b.p. 92° to 96°) was obtained in an average yield of 43 per cent, and di*iso*propyl ketone (b.p. 122° to 127°) in 10 to 15 per cent yield. Redistillation of the methyl *iso*propyl ketone gave a main fraction, b.p. 93° to 95°, n_D^{20} 1·3882.

After 8 mol of *iso*butyric acid had passed through the tube the thoria was regenerated by passing first air and then oxygen, while the temperature of the tube was gradually raised to 550°.

Preparation of 2 : 3-*Dimethylpentan*-3-*ol.*

To a solution of ethyl magnesium chloride [prepared from 96 g (4 g atoms) of fine magnesium turnings and 290 cc (4 mol) of ethyl chloride in 550 cc of anhydrous ether, with the addition of 0·5 cc of bromine as catalyst], was added slowly 350 cc (3·25 mol) of methyl *iso*propyl ketone in an equal volume of ether; the vessel was well cooled in ice and vigorously stirred throughout the addition. At the end of the addition, the ice was replaced by warm water and the ether allowed to reflux for a while.

After having stood overnight, the mixture was decomposed with 20 per cent sulphuric acid. The ether layer was separated, washed with water, then with sodium bicarbonate solution and finally twice more with water. The ethereal solution was dried over anhydrous sodium sulphate and the ether evaporated on a water-bath.

The residue was distilled under reduced pressure, yielding 296 cc of carbinol, b.p. 53° to 54°/22 mm, n_D^{20} 1·4284 (66 per cent yield).

Dehydration of 2 : 3-*dimethylpentan*-3-*ol.*

The carbinol was refluxed with iodine for 2 hr and the product distilled slowly through a Dufton column. A mixture of olefin and water came over between 75° and 97°. The water was separated and the olefin dried over sodium sulphate: it gave a negative Beilstein test for halogen. The olefin was distilled from sodium, giving 175 g (83 per cent yield) of a fraction, b.p. 90° to 94·5°, n_D^{20} 1·4139, a mixture of 2 : 3-dimethylpentenes.

2 : 3-*Dimethylpentane.*

250 cc of purified methyl alcohol* were added to the olefin and the solution was hydrogenated (in a 1400-cc capacity Baskerville and Lindsay hydrogenator) under a maximum hydrogen pressure of 100 atm and a temperature of 200° using Raney nickel as catalyst. The absorption of hydrogen was slow. The product, washed four times with water to remove alcohol, had a rather high refractive index, n_D^{20} 1·3940, and slowly decolorized permanganate, indicating the presence of unchanged olefin. It was then reduced again without a solvent in two batches (in a hydrogenator of 200 cc capacity) at 90 atm and 160°. The new product twice distilled from sodium through a 90-cm Dufton column gave finally 150 cc of 2 : 3-dimethyl-

* It was realized later that the frequent failure of reductions carried out in synthetic methanol solution might be due to the presence of metallic impurities arising in the manufacture of the alcohol.

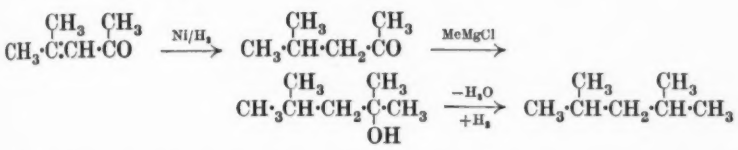
pentane, b.p. 89·6° to 89·65°/760 mm (corr), n_D^{20} 1·3920. Only small amounts of head and tail fractions had to be rejected.

	B.p., ° C.	n_D^{20}.
Cf. Chavanne and de Graef [9]	90·0	1·3918
Edgar, Calingaert, and Marker [1]	89·7	1·3920
Wibaut *et al.*[3]	89·8	1·3921
A.P.I. Tables give	89·79	1·39200

E. R. W.
J. C. S.

2 : 4-Dimethylpentane.

Reaction scheme :—



Methyl iso*Butyl Ketone.*

Diacetone alcohol was dehydrated by distilling with 0·5 per cent of iodine and the resulting mesityl oxide was reduced with hydrogen and Raney nickel at a low temperature and a maximum pressure of 100 atm. The pure methyl *iso*butyl ketone boiled at 118°.

2 : 4-*Dimethylpenta-2-ene.*

Into an ether solution of methyl magnesium chloride cooled in ice-water was run a mixture of equal volumes of ether and methyl *iso*butyl ketone, at the rate of 1 drop per sec, with vigorous stirring. The amount of ketone added was rather less than equivalent to the Grignard reagent. The carbinol was isolated as usual, but it decomposed slightly when distilled at atmospheric pressure. The distillate was therefore not purified but was dehydrated with iodine to yield the olefin, which, after treatment with sodium wire, was halogen-free and boiled at 82·4° to 82·8°. Chavanne and de Graef [9] showed that dehydration of 2 : 4-dimethylpentan-2-ol gave exclusively 2 : 4-dimethylpent-2-ene.

2 : 4-*Dimethylpentane.*

For hydrogenation the olefin was dissolved in purified methyl alcohol to increase the bulk for efficient stirring, and was hydrogenated at 160° and 100 atm using a Raney nickel catalyst. The product was thoroughly washed with water, dried with sodium sulphate, and refluxed with sodium wire. On fractionation two fractions were collected : (1) b.p. 80·4° to 80·5°/760 mm, and n_D^{20} 1·3822; (2) b.p. 80·5° to 80·6°/760 mm, and n_D^{20} 1·3822. Egloff [8] gives b.p. 80·8° and n_D^{20} 1·3824. A.P.I. Tables give b.p. 80·51° and n_D^{20} 1·38150.

E. R. W.

OCTANES.

By F. R. Buck, B. B. Elsner, T. Henshall, S. H. Morrell, T. S. Moore, G. Müller, A. R. Murray, J. C. Smith, and E. R. Wallsgrove.

2-Methylheptane.

Two new syntheses of this hydrocarbon have been developed. The first employs methyl *n*-amyl ketone, a pure specimen of which was available :—

$$n\text{-}C_5H_{11}\cdot CO \xrightarrow[H_2O]{MeMgCl} n\text{-}C_5H_{11}\cdot C(CH_3)(OH) \xrightarrow{-H_2O} n\text{-}C_4H_9\cdot CH{:}C(CH_3) \xrightarrow{H_2/Ni} CH_3\cdot(CH_2)_4\cdot CH(CH_3)$$

That the olefin obtained is in fact 2-methylhepta-2-ene follows from the direct synthesis of the isomeric 2-methylhepta-1-ene by interaction of *n*-butyl magnesium chloride and β-methallyl chloride :—

$$CH_3\cdot(CH_2)_3\cdot MgCl + ClCH_2\cdot C(CH_3){:}CH_2 \longrightarrow CH_3\cdot(CH_2)_4\cdot C(CH_3){:}CH_2.$$

The constants of this olefin are quite different from those of the dehydration product of 2-methylheptan-2-ol; both olefins on reduction yield the same paraffin.

2-Methylheptan-2-ol.

Into a 2-litre, three-necked flask fitted with an inlet tube, stirrer, and double-surface condenser were placed 48 g of magnesium turnings, and on to this was poured a solution of 10 g of methyl iodide in 100 cc of dry ether. When the reaction had started 600 cc of dry ether were added and a rapid stream of methyl chloride gas was passed in with stirring until the whole of the magnesium had dissolved. The flask was then surrounded with a freezing-mixture, and a solution of 228 g of methyl *n*-amylketone in 200 cc of ether was added dropwise. From this mixture there were obtained 171 g (66 per cent yield) of 2-methylheptan-2-ol, b.p. 70°/20 mm, and 47 g of a self-condensation product of the methyl *n*-amylketone.

2-Methylhepta-2-ene.

The heptanol was heated with iodine (0·5 per cent) for 2 hr at 140°, after which the mixture was slowly distilled through a column. The olefin obtained (yield 90 per cent) boiled at 121·5° to 121·7°/755 mm, n_D^{20} 1·4168. (Found : Iodine Number, 226; calc 227). Kishner [11] gives for the olefin obtained from methyl heptenone,

$$CH_3\cdot C(CH_3){:}CH\cdot(CH_2)_2\cdot CO\cdot CH_3 \longrightarrow CH_3\cdot C(CH_3){:}CH\cdot(CH_2)_3\cdot CH_3,$$

the values b.p. 122·4°/756 mm and n_D^{20} 1·4169.

2-Methylhepta-1-ene.

190 g of β-methallyl chloride (1·5 mol) were slowly added to the cooled Grignard reagent prepared from 130 g of *n*-butyl chloride and 33·7 g of magnesium. After addition of water and acid, the ether layer was washed with bicarbonate solution, with water, dried, and fractionated. A fraction of b.p. 117° to 119° was purified by refluxing for 2 hr with methyl-alcoholic potash solution. The olefin, washed with water, dried, and distilled from sodium, had b.p. 118·2° to 118·8° and n_D^{20} 1·4143. Egloff [8] (quoting a thesis of Mavity and Boord) gives b.p. 119·2° to 119·5° and n_D^{20} 1·4122.

2-Methylheptane.

(*a*) Hydrogenation of 2-methylhepta-2-ene at 100° and 75 atm with Raney nickel as catalyst gave the paraffin of b.p. 116·8° to 117·0°/743 mm, n_D^{20} 1·3950.

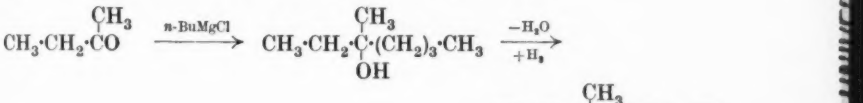
(*b*) Hydrogenation of 2-methylhepta-1-ene with hydrogen at 60 atm and Raney nickel proceeded in the cold, and the temperature was raised to 100° at the finish. The product had b.p. 117·0°/748 mm and n_D^{20} 1·3951.

Repetition on a large scale of the preparation from methyl *n*-amylketone gave 2100 cc of 2-methylheptane, b.p. 117·3° to 117·5°/760 mm, n_D^{20} 1·3950. Egloff [8] gives b.p. 117·2°/760 mm and n_D^{20} 1·3947. A.P.I. Tables give b.p. 117·645° and n_D^{20} 1·39495.

T. H. B. B. E.
J. C. S.

3-Methylheptane.

The method employed for the preparation of 3-methylheptane was that used by Wibaut and co-workers,[2] except that the cheaper *n*-butylchloride was substituted for the bromide and that the dehydration of 3-methylheptan-3-ol was carried out with phosphorus pentoxide.



3-Methylheptan-3-ol.

20 mol of *n*-butylchloride were converted into *n*-butyl magnesium chloride in 2- and 3-mol runs, and the Grignard reagent was coupled with methyl ethyl ketone using 5 per cent less ketone than the theoretical amount. After decomposition of the Grignard complex the reaction product was fractionated through a Young column under reduced pressure. In various preparations the following boiling points were obtained :—

Mm.	B.p., ° C.
23	75·1
55	90·5
84	100·0
758	163·8

The value for 758 mm was obtained by redistillation of two separate smaller amounts of the carbinol at normal pressure using a Dufton column. In

both cases most of the carbinol distilled at 163·8° and there was no perceptible decomposition to water and olefine. The refractive index of all fractions was n_D^{20} 1·4285, and the average yield was 69 per cent.

Dehydration of the Carbinol.

Use of phosphorus pentoxide gives a high yield of the expected mixture of olefins. The carbinol was placed in a wide-necked, conical flask surrounded with a freezing mixture at −15°. Phosphorus pentoxide was added in small quantities, the reaction mixture being stirred mechanically. Dehydration was complete in 1½ hr and the olefin mixture was poured off. The pentoxide layer was then decomposed with ice-water, the organic layer run off, dried with sodium sulphate, and added to the main fraction. (The smell and colour indicated the presence of some polymerized material.) Distillation yielded a main fraction of b.p. 121° to 122° and a residue of polymers boiling up to 240°.

3-*Methylheptane.*

The olefin mixture, b. p. 121° to 122°, reduced with Raney nickel and hydrogen at 170° and 100 atm gave a main fraction of paraffin, b.p. 118·6°/760 mm, n_D^{20} 1·3983. Wibaut *et al.*[2] give b.p. 118·9°, n_D^{20} 1·3986; Smittenburg *et al.*[12] give b.p. 119·1°, n_D^{20} 1·3980. A.P.I. Tables give b.p. 118·927° and n_D^{20} 1·39849.

F. R. B.
B. B. E.

4-Methylheptane.

The numerous references to this hydrocarbon give no suitable method for its preparation in quantity.

Clarke [13, 13a] prepared a *sec*-amylacetoacetic ester, which gave 4-methylheptan-2-one on ketonic hydrolysis. The ketone was then reduced to the corresponding carbinol, which was converted to the iodide, and the latter reduced to the hydrocarbon with iron and hydrochloric acid.

Levene and Marker [14] prepared *sym*-dipropylmethylmethane from *l*-methylpropylpropionic acid, by condensing 2-bromopentane with malonic ester and resolving the cinchonidine salt of the product. The ethyl methylpropylpropionate was reduced with sodium and alcohol to the corresponding carbinol, which was converted via the bromide, cyanide, etc., into the octane.

Bjelouss [15] obtained 4-methylhepta-3-ene-5-ol by the Grignard reaction between ethyl magnesium bromide and methylethylacrolein. Reduction of the double bond, conversion into the bromide, and removal of hydrogen bromide with pyridine, then gave 4-methylhepta-3-ene (b.p. 115° to 120°).

The scheme of our present preparation was as follows:—

$$\begin{matrix}CH_3\\ CO{\cdot}O{\cdot}C_2H_5\end{matrix} + 2CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}MgCl \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

$$\xrightarrow[+H_2]{-H_2O} CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\displaystyle CH_3}{CH}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

4-Methylheptan-4-ol.

Propyl chloride and commercial ethyl acetate were thoroughly dried and fractionated. The Grignard reaction (1·8 mol of ester, 4 mol of propyl chloride, and 1500 cc of ether) was carried out without cooling, and yielded 58 per cent of carbinol, b.p. 160° to 160·5°, n_D^{20} 1·4258.

4-Methylhepta-3-ene.

The carbinol was dehydrated with phosphorus pentoxide (ice cooling). Fractional distillation of the mixture of geometrical isomers (700 cc) gave the following results :—

°C.	Cc.	n_D^{20}.
Up to 117	40	—
117·0 to 117·8	70	1·4171 *
117·8 to 118·2	75	1·4174
118·2 to 118·4	80	1·4173 *
118·4 to 118·6	100	1·4180
118·6 to 118·9	100	1·4180 *
118·9 to 119·3	175	1·4180

(The fractions marked * showed no difference among themselves when examined by means of the infra-red spectroscope.)

4-Methylheptane.

The hydrogenation was carried out in the usual way at 160° and 80 atm pressure of hydrogen. The final distillation yielded a constant-boiling main fraction of 450 cc, b.p. 117·5°/760 mm, n_D^{20} 1·3980. A.P.I. Tables give b.p. 117·712° and n_D^{20} 1·39792.

G. M.
B. B. E.

3-Ethylhexane.

Clarke and Riegel [16] prepared 3-ethylhexan-3-ol from diethyl ketone and propyl magnesium iodide; by treatment with iodine and red phosphorus, the carbinol was converted into the iodide, which was transformed into the olefin and this reduced to the paraffin with nickel and hydrogen at 180°. The last three stages gave only very small yields.

More recent references [17, 17a, 17b] to this hydrocarbon were concerned with its physical properties, and did not mention the method of preparation.

In the present synthesis, the first stage of Clarke's method was followed, but using propyl magnesium chloride in place of the iodide. Dehydration of the carbinol was obtained with phosphorus pentoxide, and the resulting olefins were reduced with hydrogen, and Raney nickel :—

$$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}MgCl \longrightarrow CH_3{\cdot}CH_2{\cdot}\underset{\displaystyle OH}{\overset{\displaystyle CH_2{\cdot}CH_3}{\overset{|}{C}}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

$$\xrightarrow[+H_2]{-H_2O} CH_3{\cdot}CH_2{\cdot}\overset{\displaystyle CH_2{\cdot}CH_3}{\overset{|}{C}}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

3-Ethylhexan-3-ol.

The flask containing the Grignard compound was cooled to 0° in ice and salt, and a dilute solution of diethyl ketone in ether (1 : 3) was added very

slowly (1 drop in 2 sec). The reaction mixture was refluxed for 4 hr and allowed to stand overnight. In this way, the yield of carbinol could be increased to 55 per cent; the average yield of several runs was 48 per cent. About 20 per cent of the diethyl ketone was recovered unchanged, and about 25 per cent formed a polymerized residue. The boiling point of 3-ethylhexan-3-ol is 158°/760 mm (decomposition taking place to a very small extent), and 98° to 100°/100 mm, 110° to 112°/160 mm; n_D^{20} 1·4310.

3-*Ethylhexa*-2-*ene*.

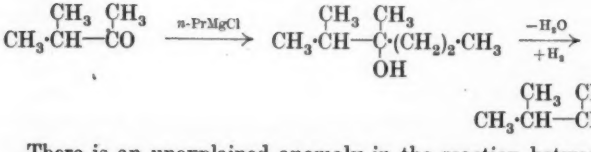
The carbinol was cooled in ice-water, and three-quarters of its weight of phosphorus pentoxide was slowly added with stirring. The olefins were decanted, and the paste of phosphoric acid and phosphorus pentoxide dissolved in water. The olefin layer of the latter portion was separated, washed with water and sodium bicarbonate solution, and dried before it was combined with the main part to be fractionated through a Stedman column of 25 plates. 440 cc of a liquid of b.p. 119·4° to 119·8°, n_D^{20} 1·4210, were obtained. The refractive index and boiling point of the main fraction indicate that the dehydration with phosphorus pentoxide produced only a very small percentage of 3-ethylhexa-3-ene (b.p. 112·5°, n_D^{20} 1·4149). The physical constants of 3-ethylhexa-2-ene (mixture of geometrical isomers) quoted in the literature are b.p. 119·6° to 120·5°, n_D^{20} 1·4246.

3-*Ethylhexane*.

The fractions of b.p. 119° to 120° were united and then hydrogenated at 85 atm pressure of hydrogen and a temperature of 160°, using Raney nickel as catalyst. The product was purified in the usual manner and fractionated through a 25-plate Stedman column. The main fraction (about 400 cc) boiled constantly at 118·5°/760 mm (corr), n_D^{20} 1·4018. A.P.I. Tables give b.p. 118·537° and n_D^{20} 1·40162.

G. M.
B. B. E.

2 : 3-DIMETHYLHEXANE.



There is an unexplained anomaly in the reaction between ketones and Grignard reagents. Whitmore and Evers [18] reported that when a series of Grignard reagents reacted with methyl *iso*propyl ketone there was a minimum yield of carbinol with *n*-propyl magnesium chloride :—

EtMgCl, 59 per cent; *n*-PrMgCl, 35 per cent; *n*-BuMgCl, 61 per cent; *n*-C_5H_{11}MgCl, 60 per cent.

2 : 3-*Dimethylhexan*-3-*ol*.

In our preparation of this carbinol it was found necessary to cool with ice and salt in order to obtain even a 30 per cent yield of carbinol. When higher temperatures were used the product distilled over a wide range.

A solution of *n*-propyl chloride (353 cc, 4 mol) in 450 cc of ether was added slowly to 96 g (4 g atoms) of magnesium and 550 cc of ether, the reaction being started with a drop of bromine. To the resulting solution of *n*-propyl magnesium chloride, methyl *iso*propyl ketone (327 g, 3·8 mol, b.p. 92° to 92·5°, n_D^{20} 1·3882) in 400 cc of ether was added slowly with efficient stirring while the flask was cooled with an ice–salt mixture. The carbinol (300 cc) isolated in the usual manner boiled at 64° to 70°/25 mm, n_D^{20} 1·431. Previous experiments had shown that it was wasteful to attempt to isolate a pure product by fractional distillation.

2 : 3-*Dimethylhexane.*

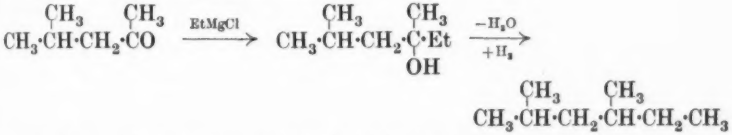
Dehydration of the carbinol by refluxing with iodine for 2½ hr and then distilling slowly gave a mixture of olefins. Distilled from sodium the mixture boiled at 113·5° to 118°, and n_D^{20} varied from 1·4200 to 1·4226. Reduction with Raney nickel and hydrogen at 150 to 100 atm and 150° gave a product (stable to permanganate solution), b.p. 115·4° to 115·65°/761 mm, n_D^{20} 1·4012. Wibaut *et al.*[2] give b.p. 115·8°, n_D^{20} 1·4015. Smittenberg [3] give 115·8° and 1·40131 respectively. A.P.I. Tables give b.p. 115·61° and n_D^{20} 1·40138.

E. R. W.

2 : 4-Dimethylhexane.

The method applied is recorded by A. Meyer and M. Tuot [19] except that the cheaper ethyl chloride was substituted for the bromide.

The reaction scheme is as follows :—



Mesityl oxide was prepared by the dehydration with iodine of diacetone alcohol.

Methyl iso*butyl ketone* was prepared by hydrogenation of mesityl oxide with Raney nickel as catalyst. For rapid hydrogenation it was necessary to free the mesityl oxide completely from iodine. This was effected by refluxing with 5 per cent of its weight of a rather old sample of Raney nickel for ½ hr and then distilling.

2 : 4-*Dimethylhexan*-4-*ol.*

Dry ethyl chloride was bubbled slowly into a mixture of magnesium (240 g) in dry ether (1500 cc) to which 30 cc of ethyl bromide had been added to start the reaction. The passage of gas was continued until all the magnesium had disappeared.

The Grignard reagent was surrounded by a freezing mixture, and a solution of methyl *iso*butyl ketone (1140 cc) and dry ether (700 cc) added slowly under vigorous stirring. The product was decomposed with ice and then with ice-cold 10 per cent sulphuric acid. The ether layer was washed with water, dried, and after removal of the ether, the residual oil was distilled under reduced pressure. The alcohol distilled (b.p. 64°/25

mm; Bodroux and Taboury [20] give b.p. 151° to 153°/750 mm) as a colourless oil having a terpene-like odour. (Yield 90 per cent.)

2 : 4-*Dimethylhexa-(?)-4-ene.*

The alcohol was dehydrated by slow distillation with 0·5 per cent of iodine. The upper layer was removed, washed with water, with thiosulphate solution, again with water, dried over sodium sulphate, and fractionally distilled over sodium. It boiled at 110° to 112°/760 mm, yield 96 per cent. Tuot [19a] gives b.p. 109°/737 mm.

2 : 4-*Dimethylhexane.*

The olefin was hydrogenated under a pressure of 120 atm and at a temperature of 100° C with Raney nickel as catalyst. The hydrocarbon was washed with water, dried over sodium sulphate and finally distilled from sodium. A sample of 2100 cc of hydrocarbon was prepared having the following constants: b.p. 108·4° to 108·5°/746 mm, n_D^{20} 1·3954. Meyer and Tuot [19] give b.p. 108°/750 mm, n_D^{20} 1·3950. Maman, [17b] gives b.p. 109°/760 mm, n_D^{20} 13952. A.P.I. Tables give b.p. 109·432° and n_D^{20} 1·39534.

T. H.
J. C. S.

2 : 5-Dimethylhexane.

Hitherto this hydrocarbon has been prepared by the Wurtz–Fittig reaction from *iso*butyl bromide or iodide. [12, 21, 22] A much simpler method, however, and one which lends itself to larger-scale preparation has been found, which uses as starting material the easily accessible reagent, β-methallyl chloride.

Miukhailenko and Protasova [23, 23a] report the conversion of benzyl chloride to diphenylethane in theoretical yield by treating its ether solution with magnesium and 0·01 to 0·04 mol of anhydrous ferric chloride, ferric bromide, cupric chloride, or mercuric bromide. Absence of catalyst lowers the yield to 60 per cent. This result, together with the known tendency of allyl halides and other halides containing a highly reactive halogen atom, to yield considerable quantities of hydrocarbons by Wurtz-type coupling in the Grignard reaction, suggested that such a reaction would be successful with the highly reactive β-methallyl chloride. Such a conclusion was amply borne out in practice; the reaction producing an 86 per cent yield of 2 : 5-dimethylhexa-1 : 5-diene.

The reaction scheme may be represented as follows:—

$$2CH_2{:}\overset{\displaystyle Me}{\overset{|}{C}}{\cdot}CH_2Cl + Mg\ (\text{in } Et_2O + FeCl_3) \longrightarrow$$

$$CH_2{:}\overset{\displaystyle Me}{\overset{|}{C}}{\cdot}CH_2{\cdot}MgCl + Cl{\cdot}CH_2{\cdot}\overset{\displaystyle Me}{\overset{|}{C}}{:}CH_2 \xrightarrow{-MgCl_2} CH_2{:}\overset{\displaystyle Me}{\overset{|}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\displaystyle Me}{\overset{|}{C}}{:}CH_2$$

It was found that the 2 : 5-dimethylhexa-1 : 5-diene always contained some halide, sufficient to poison the nickel catalyst used in the reduction; a halogen-free product was obtained by refluxing the impure diene with methyl alcoholic potash for 4 hr.

After work on this hydrocarbon had been begun a paper appeared from the laboratories of the Shell Development Co. in the U.S.A. [24] on the reactions

of β-methallyl chloride in which the coupling reaction without the use of ferric chloride is described. Although these authors claim a 90 per cent yield by their technique, their results could not be repeated.

2 : 5-Dimethylhexa-1 : 5-diene.

Procedure A. Into a 3-litre, three-necked flask, fitted with an efficient, sealed stirrer, and two long, double-surface condensers, were placed 48 g of magnesium turnings and 362 g (or 389 cc) of β-methallyl chloride (b.p. 72·2°) in 800 cc of dry ether. The stirrer was set in motion, and anhydrous ferric chloride (13 g) was added. Reaction soon set in; at this stage the stirrer was stopped, and the very vigorous reaction controlled by playing a stream of cold water on the flask. The reaction mixture soon developed a pink tinge, and magnesium chloride separated out continuously. When the reaction subsided the pink coloration slowly disappeared, until at the finish, the colour was white, from magnesium chloride.

The mixture was then refluxed for a further ½ hr to complete the reaction, and then, after cooling, was decomposed by cautious addition of water which served to dissolve most of the magnesium chloride. When sufficient water had been added to produce two distinct layers, the ether layer was run off. The lower layer was washed twice again with ether; the ether extracts were combined, washed with water, dried over sodium sulphate, and distilled through a column.

The first fraction <40° was mostly ether; the second, from 40° to 75°, was principally chloride with some diene, and the fourth, boiling at 110° to 115° C was the diene. The yield was 200 g of a colourless, highly refractive liquid.

This diene was purified by refluxing with methyl alcoholic potash (400 cc of hydrocarbon and 60 g of potassium hydroxide in 400 cc of methyl alcohol). The diene thus treated was washed, dried, and distilled. It was halogen-free, and the main fraction boiled at 114·2°/760 mm, n_D^{20} 1·4292.

Procedure B. A solution of bromine (1 cc) in ether (150 cc) was poured on to magnesium (72 g) in the 3-litre flask, and then a solution of β-methallyl chloride (585 cc) in ether (1000 cc) was added from a dropping funnel through the condenser at such a rate that the reaction was easily controlled. The reaction always began immediately and the yields of diene were between 85 and 95 per cent.

2 : 5-Dimethylhexane.

The diene was hydrogenated at 100° C under a pressure of 100 atm with Raney nickel as catalyst.

The product, purified by shaking with alkaline permanganate, was washed, dried, and distilled (over sodium). It was then placed in the Dufton distilling apparatus, clean sodium added, and fractionation started. A few drops passed over below 108·1°, and there was a small fraction 108·1° to 108·9°, n_D^{20} 1·3927 (65 cc): these were rejected. The main fraction (2250 cc) boiled at 108·9° to 109·1°/760 mm, and had n_D^{20} 1·3929 to 1·3930.

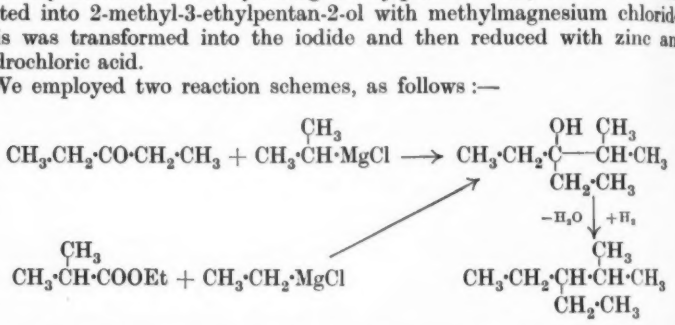
Smittenberg *et al.*[12] give b.p. 109·3°/760 mm, n_D^{20} 1·3930. A.P.I. Tables give b.p. 109·15° and n_D^{20} 1·39246.

T. H. B. B. E.
J. C. S.

2-Methyl-3-Ethylpentane.

2-Methyl-3-ethylpentane was synthesized by Clarke,[25] ketonic hydrolysis of diethylacetoacetic ester yielding 3-ethylpentan-2-one, which was converted into 2-methyl-3-ethylpentan-2-ol with methylmagnesium chloride. This was transformed into the iodide and then reduced with zinc and hydrochloric acid.

We employed two reaction schemes, as follows :—



In the first method, however, using diethyl ketone, a yield of only 28 per cent of the carbinol was obtained. The low yield was undoubtedly due to the use of a branched-chain Grignard reagent, resulting in reduction and condensation of the ketone.[26] In addition, a considerable amount of unchanged ketone was recovered. The second method, on the other hand, gave a 78 per cent yield of carbinol.

2-Methyl-3-ethylpentan-3-ol.

The addition of the methyl *iso*butyrate to ethyl magnesium chloride (3 mol) was carried out at such a rate that the ether refluxed rapidly. The physical constants of the product were as follows: b.p. 160°/760 mm, 93°/100 mm, 85° to 86°/60 mm, n_D^{20} 1·4367. (Grigorovitch and Pavloff[27] give b.p. 159·5° to 161°/750 mm.)

[An attempt to couple methyl methacrylate with ethyl magnesium chloride by cooling in a freezing mixture and adding the ester at a very slow rate, yielded only a small amount of the unsaturated carbinol, most of the substance being transformed into a polymerized elastic jelly of greyish-white colour.[28] The resulting carbinol was dehydrated with anhydrous copper sulphate, when it gave a mixture of diolefins boiling over a wide range (about 20° in vacuum); this part of the research was therefore discontinued.]

2-Methyl-3-ethylpenta-2-ene.

The dehydration of the carbinol was carried out with phosphorus pentoxide under ice-cooling, and yielded well over 90 per cent of the olefin mixture. This liquid (about 900 cc) started to boil at 110° and distilled with only one appreciable halt up to 117·5°; a fraction (200 cc) of b.p. 115·0° to 115·5°/752 mm had refractive index, n_D^{20} 1·4227. The literature gives for the boiling point of 4-methyl-3-ethylpenta-2-ene (mixture of geometrical isomers) 114·5° to 116·5° (Boord,[29] but Reid, *Ohio State Univ. Thesis*, 1938, quoted by Doss [30]) gives b.p. 113·8° to 114·8°; n_D^{20} 1·4199.

One fraction of boiling range 116·2° to 117° was refractionated, when it gave a constant-boiling fraction (at 117·0°, n_D^{20} 1·4247), which according to

spectroscopic evidence was pure 2-methyl-3-ethylpenta-2-ene. Nasarov [31] found for this olefin b.p. 113° to 116·5°, and Reid quoted by Egloff,[8] gives b.p. 117·3°, n_D^{20} 1·4246. Dr H. W. Thompson kindly examined the specimens by infra-red spectroscopy.

2-Methyl-3-ethylpentane.

The olefin fractions were united and reduced at 160° and 85 atm pressure of hydrogen, using a Raney nickel catalyst. A constant-boiling fraction (550 cc) was obtained, b.p. 115·4°/760 mm, n_D^{20} 1·4041 (compare Calingaert and Edgar [32] and Maman [17b]). A.P.I. Tables give b.p. 115·653° and n_D^{20} 1·40402.

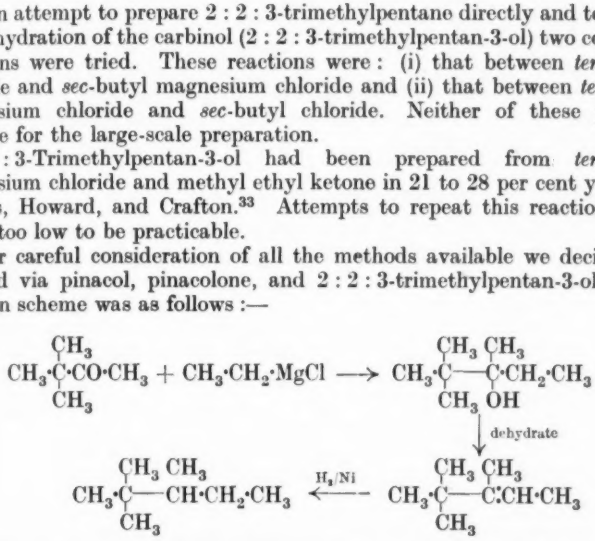
G. M.
B. B. E.

2 : 2 : 3-Trimethylpentane.

In an attempt to prepare 2 : 2 : 3-trimethylpentane directly and to avoid the dehydration of the carbinol (2 : 2 : 3-trimethylpentan-3-ol) two coupling reactions were tried. These reactions were: (i) that between *tert*-butyl chloride and *sec*-butyl magnesium chloride and (ii) that between *tert-butyl* magnesium chloride and *sec*-butyl chloride. Neither of these proved suitable for the large-scale preparation.

2 : 2 : 3-Trimethylpentan-3-ol had been prepared from *tert*-butyl magnesium chloride and methyl ethyl ketone in 21 to 28 per cent yield by Brooks, Howard, and Crafton.[33] Attempts to repeat this reaction gave yields too low to be practicable.

After careful consideration of all the methods available we decided to proceed via pinacol, pinacolone, and 2 : 2 : 3-trimethylpentan-3-ol. The reaction scheme was as follows:—



Whitmore and Laughlin [34] found that on dehydration by heating with iodine, 2 : 2 : 3-trimethylpentan-3-ol underwent partial rearrangement, yielding 80 per cent of the "normal" product 2 : 2 : 3-trimethylpenta-3-ene and 20 per cent of the rearranged product, 2 : 3 : 3-trimethylpenta-1-ene.

Wibaut [2] tried various other methods of dehydration to see whether this change in the carbon skeleton could be avoided. He found that, whatever method was tried, a mixture of the two olefins was produced. The boiling points are close and the olefins are very difficult to separate by fractional distillation. Whitmore and Laughlin [34] give the values:—

2 : 2 : 3-trimethylpenta-3-ene, b.p. 111·9°/760 mm; n_D^{20} 1·4232
2 : 3 : 3-trimethylpenta-1-ene, b.p. 108·2°/760 mm; n_D^{20} 1·4178.

On hydrogenation of the olefin mixture, 2 : 2 : 3- and 2 : 3 : 3-trimethylpentane are obtained; the boiling points of these are also close together, 110·2° and 113·6° respectively.

In the hope that a low-temperature dehydration would avoid the rearrangement (all the other methods of dehydration required heating) dehydration at 0° with phosphorus pentoxide was tried; but the boiling point and refractive index of the olefin and of the paraffin subsequently obtained showed that some rearrangement had taken place, and careful fractionation was necessary.

Preparation of Pinacolone.

Pinacol was prepared from acetone by the procedure given in *Organic Syntheses*.[35] It was found that 1½ times the quantities given in ref 35, p. 448 could conveniently be taken in a 5-litre flask. 17·5 litres of acetone gave 8 kg of pinacol hydrate. The dryness of the actone was found to be the factor controlling the time required for the reaction to start; when the acetone was thoroughly dried the reaction started at once in the cold.

The rearrangement to pinacolone was carried out by distilling the pinacol hydrate rapidly with 6*N*-sulphuric acid. Ref. 35, pp. 451, 452. 8 kg of pinacol hydrate gave 2 litres of pinacolone, b.p. 104° to 108° (main fraction 105° to 106°), n_D^{20} 1·3977.

Preparation of 2 : 2 : 3-*trimethylpentan*-3-*ol.*

Ethyl magnesium chloride was prepared on a 10-mol scale by adding 800 cc of ethyl chloride in 800 cc of anhydrous ether to 240 g of magnesium turnings and 1000 cc of ether, with a few drops of bromine to catalyse the reaction. To the ethereal solution of ethyl magnesium chloride, 700 cc of ether were added and then a solution of 1000 cc of pinacolone in 1000 cc of ether was run in slowly with vigorous stirring, the reaction vessel being well cooled in ice. The carbinol was then isolated in the usual manner. 2 : 2 : 3-Trimethylpentan-3-ol of b.p. 68° to 72°/40 mm, n_D^{20} 1·4352, was obtained in a yield of about 50 per cent.

Dehydration of 2 : 2 : 3-*trimethylpentan*-3-*ol.*

To 500 cc of the carbinol in a conical beaker (well cooled in ice and the contents vigorously stirred) 325 g of phosphorus pentoxide were added in portions. The completion of the reaction was shown by disappearance of the distinctive carbinol smell. The stirring was continued for another 30 min and the mixture was then left overnight. The olefin was decanted on to a little fresh phosphorus pentoxide and allowed to stand a few hours.

The olefin was then carefully fractionated; for hydrogenation, the fractions boiling between 110·9° and 111·8°, n_D^{20} 1·4225 to 1·4232 were taken.

The last fraction, between 111·6° and 111·8°, smelt of hydrogen chloride. The olefin was therefore treated with sodium wire, refluxed for a while, and then distilled. After this treatment, the olefin failed to give the Beilstein test for the presence of halogen. The olefin stands up well to sodium and does not polymerize; the faint darkening in colour from the sodium treatment was attributed to a trace of impurity.

Hydrogenation of the Olefin.

The olefin was hydrogenated in quantities of 600 to 700 cc at a time using Raney nickel as catalyst. The product was washed four times with water and dried over sodium sulphate. 2400 cc of product were obtained which did not decolourize very dilute permanganate after two days' standing. It was then refluxed with sodium wire and fractionated.

Fractionation of the Paraffin.

1200 cc of liquid were distilled from sodium through a column made of three Dufton glass spirals, with the following results (temperatures uncorrected, bar = 751 mm) :—

	B.p., ° C.	n_D^{20}.
(1)	108 to 109·6	1·4023
(2)	109·6 to 109·85	1·4034
(3)	109·85 to 110·0	1·4036
(4)	110·0 to 110·1 (= 110·6 corr)	1·4036
(5)	110·1 to 110·4	1·4037
(6)	110·4 to 110·6	1·4039
(7)	110·6 to 110·8	1·4041
(8)	110·8 to 111·2	1·4042

Distillations of the second batch of 1200 cc gave similarly a good fraction b.p. 109·9° to 110·5° corr.

The redistillation of the best fractions b.p. 109·6° to 110·6° proceeded as follows (bar 750 mm; total correction, add 0·7° C).

	B.p., ° C.	n_D^{20}.
(1)	Up to 109·4	—
(2)	109·4 to 109·5	1·4030 to 1·4031
(3)	109·5 to 109·6 to 109·7	1·4031 to 1·4032 to 1·4033
(4)	109·7 to 110·0	1·4032 to 1·4033

Final distillation of the best fractions of 2 : 2 : 3-trimethylpentane under a barometric pressure of 762 mm.

	B.p., ° C.	n_D^{20}.	Vol., c.c.
(1)	Up to 109·0	—	—
(2)	109·9 to 110·0	1·4030	80
(3)	110·0 to 110·05	1·4030	60
(4)	110·05 to 110·2	1·4031 to 1·4032	—
(5)	110·2 to 110·3	1·4035	—

As a result, about 140 cc of pure 2 : 2 : 3-trimethylpentane were obtained; b.p. 110·0° to 110·15°/760 mm corr, n_D^{20} 1·4030. The fractions 4 and 5 were together about 1500 cc.

Physical constants given by:	B.p., ° C.	n_D^{20}.
(A) Whitmore and Laughlin [34]	110·2	1·4030
(B) Wibaut [2]	110·4	1·4036
(C) Brooks, Howard, and Crafton [33]	109·84	1·40285
(D) A.P.I. Tables	109·846	1·40295

All fractions of refractive index above 1·4045 were mixed and distilled repeatedly. After accumulating the intermediates, b.p. 110·5° to 112·0°,

the fractions boiling between 111·7° and 113·5° and the residue from the fractionations were distilled at 750 mm.

	B.p., ° C.	n_D^{20}.
(1)	Up to 111·5	—
(2)	111·5 to 112·0	1·4056
(3)	112·0 to 113·6	1·4067
(4)	113·6 to 113·8	1·4070
(5)	113·8 to 114·0 and residue	1·4075

The fractions 4 and 5 which correspond in boiling point and refractive index to 2 : 3 : 3-trimethylpentane were too small to be of any use.

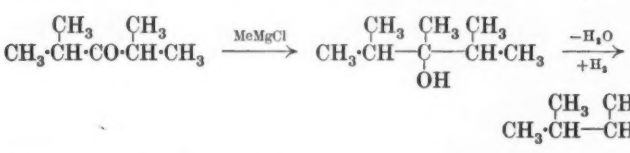
The residue was distilled through a single Dufton column. It distilled at 116°, rising to 119° and the temperature was still rising at n_D^{20} 1·4076; it smelt of 2 : 2 : 3-trimethylpentan-3-ol which apparently had escaped dehydration and also reaction with sodium. The final residue had n_D^{20} 1·4132 and was probably the carbinol.

It is claimed by P. L. Cramer and M. J. Mulligan [36] that the acetate of pinacolyl alcohol when passed over glass wool at 400° yields only 3 : 3-dimethylbuta-1-ene, and therefore attempts were made to obtain pure 2 : 2 : 3-trimethylpenta-3-ene from the acetate of the carbinol. Although a great deal of time was spent on this investigation the results were inconclusive. It was not found possible to free the acetate from unchanged carbinol and from acetic anhydride. The purest specimens of acetate on pyrolysis always gave some of the rearranged product (2 : 3 : 3-trimethylpenta-1-ene).

T. S. M. A. R. M. J. C. S.
B. B. E. E. R. W.

2 : 3 : 4-Trimethylpentane.

Three groups of workers, Whitmore and Laughlin,[37] Brooks, Howard, and Crafton,[6] and Smittenberg *et al.*[3] have recorded the physical constants of 2 : 3 : 4-trimethylpentane. Of these, only Whitmore and Laughlin [37] indicated the mode of preparation, namely :—



This was the method we adopted, but an attempt was made to obtain 2 : 3 : 4-trimethylpentan-3-ol by the interaction of *iso*propyl magnesium chloride and ethyl acetate in ether solution : only a low yield resulted.

The di-*iso*propyl ketone was obtained in 90 per cent yield by passing *iso*butyric acid (made by the reduction of methyl methacrylate followed by hydrolysis) over thoria at 400° to 430°. An attempt to avoid one stage in the process by passing methyl *iso*butyrate over the thoria catalyst at 380° to 420° gave di-*iso*propyl ketone in only 38 per cent yield.

Experimental.

Preparation of 2 : 3 : 4-*Trimethylpentan*-3-*ol.*

By the interaction of methyl magnesium chloride and di*iso*propyl ketone (b.p. 122° to 124·5°; n_D^{20} 1·3998–1·4001) in ether solution, 2 : 3 : 4-trimethylpentan-3-ol of b.p. 154° to 157°/760 mm and n_D^{20} 1·4348–1·4350 was obtained in an average yield of 53 per cent. (Stas [26] gave b.p. 156·5°/760 mm, n_D^{20} 1·4353; Whitmore and George [38] gave b.p. 101°/125 mm, n_D^{20} 1·4350).

Dehydration of 2 : 3 : 4-*Trimethylpentan*-3-*ol.*

The carbinol was dehydrated by refluxing for 3 hr with iodine and then distilling slowly. The azeotropic mixture of olefin and water came over at 85°. The olefin layer was found by the Beilstein test to contain halogen. It was therefore treated with aqueous sulphur dioxide until free from iodine, washed twice with aqueous sodium bicarbonate solution, twice with water, and dried over sodium sulphate. The olefin, distilled from sodium, gave the following fractions :—

(*a*) b.p. 110° to 112·5°, n_D^{20} 1·4224
(*b*) b.p. 112·5 to 114·5°, n_D^{20} 1·4251.

[Whitmore and Laughlin [37] reported the isolation of two olefins by fractionation :—

3-methyl-2-*iso*propylbuta-1-ene, b.p. 101·9°/741 mm, n_D^{20} 1·4083 and
2 : 3 : 4-trimethylpenta-2-ene, b.p. 114·3°/739 mm, n_D^{20} 1·4263.

They confirmed the structure of these olefins by ozonolysis.] The olefin obtained in this preparation was therefore mainly 2 : 3 : 4-trimethylpenta-2-ene.

Hydrogenation.

340 cc of olefin (fractions of b.p. 111° to 114·5°), with the addition of 100 cc of specially pure methyl alcohol to make up to sufficient volume, were hydrogenated using Raney nickel. The hydrogenation went slowly and the product, after washing four times with water to remove methyl alcohol, proved to be unsaturated, for it rapidly decolorized dilute aqueous potassium permanganate. 140 cc of the incompletely reduced substance were hydrogenated in a small (200 cc) capacity hydrogenator, without a solvent. The reduction product was washed four times with water and dried over sodium sulphate; it produced no diminution in the colour of permanganate on standing for 24 hr. The paraffin was slowly distilled from sodium through two Quickfit Dufton spirals. About 100 cc of 2 : 3 : 4-trimethylpentane, b.p. 113·3°/759 mm, n_D^{20} 1·4043, were obtained.

Physical Constants of 2 : 3 : 4-*Trimethylpentane.*

M.p., ° C.	B.p., ° C.	n_D^{20}.	d_4^{20}.
−109·97 [6]	113·39 [6]	1·40431 [6]	0·71903 [6]
—	112·8 [37]	1·4045 [37]	0·7197 [37]
—	113·4 [3]	1·4046 [3]	0·7195 [3]
	113·47	1·40195	0·71950 A.P.I.
	113·3	1·4043	Present work

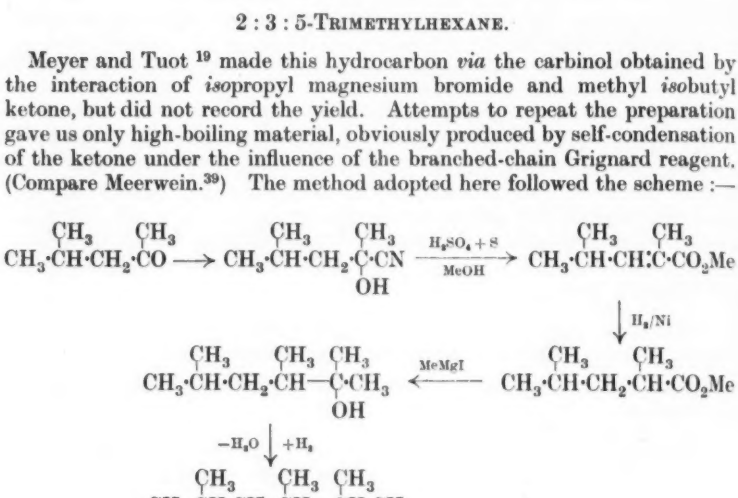
E. R. W.

2 : 3 : 5-TRIMETHYLHEXANE AND SOME DECANES.

By T. HENSHALL and E. R. WALLSGROVE.

2 : 3 : 5-TRIMETHYLHEXANE.

Meyer and Tuot [19] made this hydrocarbon *via* the carbinol obtained by the interaction of *iso*propyl magnesium bromide and methyl *iso*butyl ketone, but did not record the yield. Attempts to repeat the preparation gave us only high-boiling material, obviously produced by self-condensation of the ketone under the influence of the branched-chain Grignard reagent. (Compare Meerwein.[39]) The method adopted here followed the scheme :—



Methyl iso*butyl Ketone Cyanhydrin.*

The ketone (200 g, prepared by reduction of mesityl oxide) and a solution of potassium cyanide (130 g) in water (400 cc) were cooled in ice-water and stirred whilst 30 per cent sulphuric acid (196 g of conc acid in 720 cc of water) was added dropwise. The mixture was allowed to stand at room temperature for 4 hr; the cyanhydrin (extracted with ether) boiled at 109°/29 mm, yield 85 per cent.

Methyl-2 : 4-*dimethylpentenoate.*

A shortened route to this ester was explored, on analogy with the preparation of methacrylic ester from acetone cyanhydrin (I.C.I. patent [40]). To a mixture of methyl *iso*butyl ketone cyanhydrin (252 g, 2 mol) and sulphur (5 g) cooled with ice-water and stirred, conc sulphuric acid (294 g, 3 mol) was added slowly. The dark, viscous mass was then heated at 70° to 80° for ½ hr and then at 140° for 1 hr. After the mixture had been cooled to 60°, methyl alcohol (128 g, 4 mol) and water (72 g, 4 mol) were added and it was heated in an oil-bath at 110° for 10 hr. Addition of saturated salt solution (760 cc) to the cooled mixture precipitated an oil which, isolated with the aid of ether, boiled at 56°/10 mm or 65°/25 mm (yield 165 g, 60 per cent). (Found: C, 67·6; H, 9·8. $C_8H_{14}O_2$ requires C, 67·6; H, 9·8 per cent.) A higher-boiling fraction (b.p. 130°/25 mm) solidified on cooling and proved to be the unsaturated acid (50 g).

Methyl-αγ-dimethyl-n-valerate.

The unsaturated ester (530 cc), reduced with hydrogen and Raney nickel at 110 atm and 160°, gave a pleasant-smelling oil, b.p. 150° to 151°/760 mm, n_D^{20} 1·4070. (Found : C, 66·3; H, 11·0, $C_8H_{16}O_2$ requires C, 66·7; H, 11·1 per cent.)

2 : 3 : 5-*Trimethylhexan-2-ol.*

The ester (54 g) was added slowly to the ice-cold Grignard reagent prepared from methyl iodide (160 g) and magnesium (27 g) in ether (480 cc), and the mixture was refluxed for 2 hr, yielding finally 51 g (95 per cent) of carbinol boiling at 62° to 63°/12 mm (Found : C, 74·5; H, 13·6. $C_9H_{20}O$ requires C, 75·0; H, 13·9 per cent).

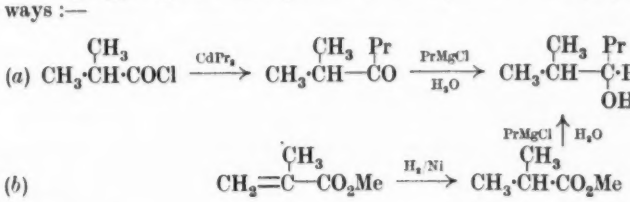
2 : 3 : 5-*Trimethylhexane.*

Dehydration of the carbinol (50 g) by heating with iodine at 130° for 4 hr gave 40 g of olefin, b.p. 129° to 130°/765 mm, n_D^{20} 1·4195. Reduction of the olefin in methanol solution with Raney nickel and hydrogen at 60° and 75 atm gave the paraffin, which had a terpene-like odour. As this was only a pilot preparation, the substance was not purified exhaustively. Distilled from sodium it boiled at 130·0° to 130·3°/745 mm and had n_D^{20} 1·4053. Meyer and Tuot [19] gave b.p. 129°/728 mm and n_D^{20} 1·4051. A.P.I. Tables give b.p. 131·37° and n_D^{20} 1·4060.

T. H.

4-*Iso*PROPYLHEPTANE.

The 4-*iso*propylheptan-4-ol required for this synthesis was prepared in two ways :—



2-*Methylhexan-3-one.*

A solution of 1·5 mol of *n*-propyl magnesium chloride was prepared by adding 120 g of *n*-propyl chloride in 150 cc of ether to 36 g of magnesium and 200 cc of ether. A further 200 cc of ether was added and the solution cooled in the ice-bath. 160 g (0·85 mol) of finely powdered anhydrous cadmium chloride (compare Gilman and Nelson [41]) were added slowly with vigorous stirring. When the addition was complete (1 hr) the ice-bath was removed and the solution stirred for 25 min. A further 200 cc of ether was added to the rather pasty mixture and the ice-bath used again while a solution of 80 g (0·75 mol) of *iso*butyryl chloride in 100 cc of ether was run in with stirring. When the addition was complete the flask was heated with hot water and the contents stirred and refluxed for 4 hr. Working up the mixture in the usual way gave 27 g (32 per cent) yield of ketone, b.p. 133° to 137°, n_D^{20} 1·4057. A second preparation (2-mol scale) gave similarly

a 34 per cent yield. The semicarbazone melted at 119°. Gilman and Nelson [41] give b.p. 129° to 132° and semicarbazone m.p. 119°.

4-Iso*Propylheptan*-4-*ol*.

(*a*) 90 g of 2-methylhexanone in 100 cc of ether were run slowly with vigorous stirring into a solution of 1 mol of *n*-propyl magnesium chloride in 400 cc of ether. Thus were obtained 68 g (54 per cent yield) of 4-*iso*propylheptan-4-ol, b.p. 96° to 98°/34 mm, n_D^{20} 1·4394. Stas [26] gives b.p. 188° to 190°/760 mm and n_D^{20} 1·4390.

(*b*) A solution of *n*-propyl magnesium chloride was prepared by the addition of 79 g (1 mol) of *n*-propyl chloride in 100 cc of ether to 24 g (1 g atom) of magnesium and 400 cc of ether. 100 cc of ether and 50 g (0·5 mol) of methyl*iso*butyrate (b.p. 92–93°, n_D^{20} 1·3830, made by reduction of methyl methacrylate) were run slowly without cooling into the Grignard reagent. Decomposition and working up in the usual manner gave 34 g (43 per cent yield) of 4-*iso*propylheptan-4-ol, b.p. 97°/30 mm, n_D^{20} 1·4386.

Altogether 162 g of the carbinol were prepared, and some 2-methylhexan-3-one was obtained from the lower-boiling fractions of the crude carbinol.

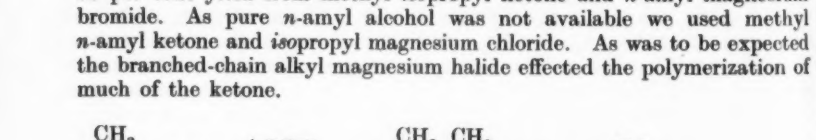
4-Iso*Propylheptane*.

34 g of the carbinol were cooled in ice-water, and 28 g of phosphorus pentoxide were added slowly with stirring; after 30 min the liquid was decanted on to a little fresh pentoxide. The first lot of pentoxide was washed with ether and the residue decomposed with ice and water. The upper layer was separated and the aqueous layer extracted once with ether. The olefin and the ether extracts were united, washed with water, dried over sodium sulphate, and the ether evaporated. On distillation from sodium the residue gave a 78 per cent yield of olefin, b.p. 152·5° to 154·5°, n_D^{20} 1·4304. Reduction at 180° and 120 atm with Raney nickel and hydrogen gave the paraffin, b.p. 158·9°/760 mm, n_D^{20} 1·4155. Butler (Dissertation, Ohio State University, 1941, quoted by Doss [30]) gives b.p. 158·6/760 mm, n_D^{20} 1·4171, and there are in the literature no other references to 4-*iso*propylheptane.

E. R. W.

2 : 3-Dimethyloctane.

2 : 3-Dimethyloctan-3-ol has been made by Whitmore and Evers [18] in 60 per cent yield from methyl *iso*propyl ketone and *n*-amyl magnesium bromide. As pure *n*-amyl alcohol was not available we used methyl *n*-amyl ketone and *iso*propyl magnesium chloride. As was to be expected the branched-chain alkyl magnesium halide effected the polymerization of much of the ketone.



2 : 3-Dimethyloctan-3-ol.

440 g (5·5 mol) of *iso*propyl chloride (b.p. 34° to 35°) in 800 cc of ether were added to 132 g (5·5 g atoms) of magnesium and 300 cc of ether. The resulting ethereal solution of *iso*propyl magnesium chloride was cooled in ice, and 500 cc of ether were added. A solution of 570 g (5 mol) of methyl *n*-amyl ketone (b.p. 148·5° to 150°, n_D^{20} 1·4090) in 800 cc of ether was added slowly with efficient stirring. The reaction product, after working up in the usual way, gave 227 g (29 per cent) of crude carbinol, b.p. 92° to 95°/18 mm and some 300 cc of high-boiling material (polymerized ketone). Redistillation of the crude carbinol gave 173 g of b.p. (103° to 105°/32 mm, n_D^{20} 1·4369). (Whitmore and Evers [18] give b.p. 69° to 70°/5 mm, n_D^{20} 1·4382.)

2 : 3-Dimethyloctane.

173 g of 2 : 3-dimethyloctan-3-ol dehydrated with 100 g of phosphorus pentoxide at 0° gave 131 g (86 per cent yield) of olefin mixture, b.p. 157° to 164·5°/750 mm and, when redistilled from sodium, b.p. 159° to 164°/750 mm, n_D^{20} 1·4319. As Whitmore and Evers record the following data :—

2 : 3-dimethylocta-3-ene, b.p. 158·6°/733 mm, n_D^{20} 1·4280
2 : 3-dimethylocta-2-ene, b.p. 161·3°/739 mm, n_D^{20} 1·4290,

our product probably contained unchanged carbinol.

Reduction of the crude olefin with Raney nickel and hydrogen at 160° to 180° and 110 atm gave the paraffin boiling at 162·2° to 164·6°, leaving 3 per cent of higher-boiling residue. Redistillation gave finally 110 cc of 2 : 3-dimethyloctane, b.p. 164·6° to 164·7°/760 mm, n_D^{20} 1·4146. Doss [30] gives b.p. 164·3°, n_D^{20} 1·4157.

E. R. W.

4 : 5-DIMETHYLOCTANE.

This previously unknown decane was made by the Wurtz reaction from 2-bromopentane :—

$$CH_3{\cdot}CHO \xrightarrow{PrMgCl} CH_3{\cdot}CH(OH){\cdot}Pr \xrightarrow{HBr} CH_3{\cdot}CHBr{\cdot}Pr \xrightarrow{Na} \begin{matrix} CH_3 & CH_3 \\ | & | \\ Pr{\cdot}CH{-}CH{\cdot}Pr \end{matrix}$$

Pentan-2-ol.

A solution of 320 g (4 mol) of *n*-propyl chloride in 400 cc of ether was added to 100 g (4·16 g atoms) of magnesium and 1200 cc of ether. The resulting ethereal solution of *n*-propyl magnesium chloride was cooled to − 5° and a solution of 132 g of acetaldehyde in 150 cc of ether was added. The resulting pentanol (199 g, 56 per cent yield) boiled at 117° to 119°, n_D^{20} 1·4067. Lauer and Stodola [42] give b.p. 117·4° to 118·9°/734 mm, n_D^{20} 1·4067.

2-Bromopentane.

199 g. of the pentanol were cooled in ice and hydrogen bromide was passed for 6 hr, the solution being then heated to 60° for 30 min. After the solution had stood overnight the process was repeated on two following days. The aqueous layer was separated and the upper layer washed four times

with water, twice with 48 per cent hydrogen bromide solution, once more with water, with sodium carbonate, and with water again. It was dried with sodium sulphate and distilled, giving 277 g (82 per cent yield) of 2-bromopentane, b.p. 116° to 117·5°, n_D^{20} 1·4412. In this way 432 g of bromide were prepared. (Literature,[43, 43a, 43b] b.p. 117—118°; n_D^{20} 1·4412.)

4 : 5-*Dimethyloctane.*

53 g of sodium wire were added to a flask containing 500 cc of ether, and 100 cc of 2-bromopentane were added in portions with shaking. The solution was allowed to stand under a reflux condenser for 24 hr, when it took on a deep blue colour. Next day 177 g of bromide in 100 cc of ether were added gradually during 2 hr, and the solution allowed to stand for 48 hr with occasional shaking. At the end of this period the flask was warmed in a water-bath at 40° for 1 hr and again allowed to stand for 24 hr. The liquid was decanted from the solid, which was then washed by decantation three times, each with 200 cc of ether. After evaporation of the mixed ethereal solutions the residue was distilled from sodium giving 28 g (21 per cent yield) of a fraction, b.p. 160° to 162·5°, n_D^{20} 1·4188. Use of powdered sodium instead of sodium wire gave only a 16 per cent yield of the decane.

41 g of the crude decane of redistillation boiled mainly at 161·6° to 162·1°/752 mm, n_D^{20} 1·4183. Final distillation with a Podbielniak column gave a main fraction of b.p. 162·2°/764 mm, n_D^{20} 1·4185. (Found : C, 84·6; H, 15·6 per cent. $C_{10}H_{22}$ requires C, 84·5; H, 15·5 per cent.)

E. R. W.

CYCLIC COMPOUNDS.

By B. B. Elsner, T. Henshall, T. S. Moore, A. R. Murray, S. H. Morrell, M. M. T. Plant, J. C. Smith, and E. R. Wallsgrove.

*cyclo*Pentane.

cyclo*Pentanone.*

The apparatus consisted of a 2-litre flask fitted with a cork carrying a wide air-condenser and a thermometer, the bulb of which came nearly to the bottom of the flask. Adipic acid (1 kg) and crystalline baryta (50 g) were placed in the flask which was then heated in an air-bath so that the temperature reached 280° in about 1 hr and remained fairly constant while *cyclo*pentanone and water slowly distilled. Finally the temperature was raised to 290° to 300°.

Solid potassium carbonate was added in order to neutralize acid which had distilled and also to salt the ketone out of the aqueous layer. The ketone layer was then dried with calcium chloride and distilled (b.p. 130°). The average yield was 440 g, or 76 per cent of the theoretical.

cyclo*Pentanol.*

The ketone was hydrogenated at 50 to 100 atm and 100° to 150° in presence of Raney nickel. The colourless, viscous oil boiled at 139° to 140°.

cyclo*Pentane*.

Dehydration of the *cyclo*pentanol was effected by a furnace reaction, the alcohol being slowly passed over alumina in an electric furnace at 300° C. The *cyclo*pentene was washed with water, dried, and distilled through a column. Hydrogenation was rapidly effected at room temperature and under 3 atm pressure employing Raney nickel as catalyst. The reaction vessel had to be cooled with a current of air from an electric fan.

The product was filtered from catalyst, washed with water, and shaken for several hours with 3 per cent alkaline permanganate. The excess permanganate was removed with SO_2, the product washed with water, dried over $MgSO_4$ and then distilled from sodium through a long Dufton column. 2500 cc were obtained of b.p. 49·3° to 49·4°/760 mm, n_D^{20} 1·4068.

Vogel [44] gives b.p. 49·3° to 49·4°/763 mm, n_D^{20} 1·40672. A.P.I. Tables give b.p. 49·264° and n_D^{20} 1·40645.

T. H.
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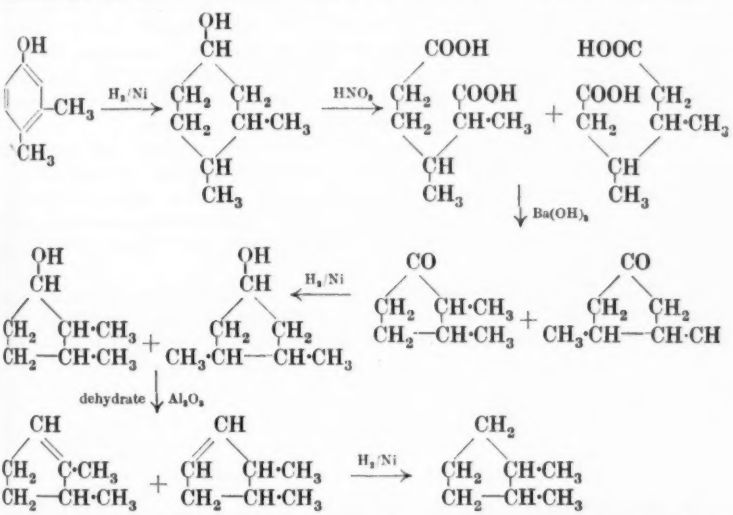
cis- and *trans*-1 : 2-Dimethyl*cyclo*pentane.

1 : 2-Dimethyl*cyclo*pentane has been obtained in *cis* and *trans* forms by several workers, and the physical constants have been determined: the two geometrical isomers differ to a surprising extent in physical properties such as boiling point (7° difference), freezing point, density, and refractive index. They have been isolated only by fractional distillation of mixtures of the two forms.

The work here described was an attempt to obtain *cis*- and *trans*-1 : 2-dimethyl*cyclo*pentane by chemical means. The reaction scheme was:—



It was hoped that it might be possible to isolate a crystalline individual *cis* or *trans* form of one of the intermediates in this synthesis.

3 : 4-Dimethylcyclohexanol.

Asymmetric ortho-xylenol (3 : 4-dimethylphenol) of m.p. 61·5°—supplied by Monsanto Chemicals Ltd.—was distilled under reduced pressure, the fraction distilling at 120°/22 mm to 131°/30 mm being collected. It was then subjected to fractional solidification : it was melted and allowed to cool down to 62°, when the mother liquor was poured off. The purified xylenol had m.p. 62° (capillary), b.p. 224° to 225°/760 mm, and 3 : 4-dinitrobenzoate, m.p. 181·5°.

The xylenol was hydrogenated using Raney nickel as catalyst under a maximum hydrogen pressure of 100 atm and at 160° to 180°. The 3 : 4-dimethyl*cyclo*hexanol boiled at 94°/23 mm, 97°/25 mm : the refractive index, n_D^{20}, of different samples varied between 1·4602 and 1·4611, mean 1·4607.

Oxidation to Dimethyladipic Acid.

The *cyclo*hexanol was oxidised with concentrated nitric acid (cf. the preparation of 1 : 3-dimethyl*cyclo*pentane). A solid oxidation product was isolated which was identified as a mixture of the two forms of βγ-dimethyladipic acid, m.p. 90° to 103°. It was not found possible to separate the two forms by fractional crystallization.

Cyclization.

The dimethyladipic acid was cyclized by heating with 10 per cent of baryta to 250° to 275°. Dimethyl*cyclo*pentanone was obtained in 84 per cent yield, b.p. 58° to 59°/20 mm, 156° to 159°/760 mm, n_D^{20} varying between 1·4354 and 1·4368. 730 cc of ketone were prepared.

The ketone was hydrogenated under a maximum hydrogen pressure of 100 atm and a maximum temperature of 210°. The product boiled over a range of 140° to 170° and gave tests for ketone, showing incomplete hydrogenation. It was therefore re-hydrogenated at a pressure of 100 atm and at 175° C. Some of the product was lost, but 415 cc of dimethyl*cyclo*pentanol boiling at 88° to 94°/54 to 55 mm were obtained, n_D^{20} 1·4430.

The dimethyl*cyclo*pentanol was dehydrated by passage through an alumina column at 300°. The olefin produced smelled of sulphide—probably from sulphate in the alumina—and to remove this, a catalyst poison, the olefin was washed with sodium hydroxide, refluxed with Raney nickel for 40 min, and then distilled : b.p. 90·5° to 97·0° (mainly 90·5° to 94·0°), n_D^{20} 1·4391.

The olefin was hydrogenated and the reduction product shown to be saturated (Baeyer test). The dimethyl*cyclo*pentane was distilled from sodium wire. As a result of repeated fractionation, there were obtained :—

		Cc.	B.p., ° C/760 mm.	M.p., ° C.	n_D^{20}.
trans :	(*a*)	20	91·7 to 91·8	—	1·4119
	(*b*)	15	91·8 to 91·9	—	1·4119
cis :	(*a*)	10	99·2 to 99·3	−68	1·4212
	(*b*)	10	99·3 to 99·4	−64	1·4212
	(*c*)	5	99·4 to 99·5	−69	1·4214

The infra-red spectra measured by Dr H. W. Thompson showed that the fractions *trans* (*a*) and *cis* (*b*) had completely different absorption curves. An intermediate fraction, b.p. 92·0° to 92·5°, n_D^{20} 1·4125, was found to show

no absorption bands due to anything other than *cis*- and *trans*-1 : 2-dimethyl*cyclo*pentane, and to be largely *trans* : it showed no bands due to either 1 : 1- or 1 : 3-dimethyl*cyclo*pentane.

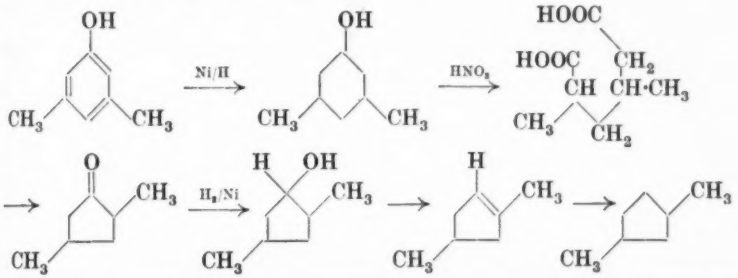
Physical Constants of 1 : 2-*Dimethyl*cyclo*pentane.*

	M.p.	B.p., ° C/760 mm.	n_D^{20}.	d_4^{20}.	Authors.
trans :	−120	91·8	—	0·7495	45
	−119	91·78	—	0·75137	46
	−119	91·8	—	—	47
	−119·25	91·89	1·4120	0·7519	A.P.I. Tables
	—	91·8	1·4119	—	Present
cis :	− 62	99·25	—	0·7718	45
	− 52·5	99·23	—	0·77268	46
	− 64	99·3	1·4212	—	Present
	—	99·25	1·4221	0·7723	A.P.I. Tables

E. R. W.

1 : 3-Dimethyl*cyclo*pentane.

This *cyclo*alkane has apparently not yet been separated into *cis* and *trans* forms. We are engaged on the problem at present, but in answer to an urgent request we prepared 3 litres of the hydrocarbon mixture. The route folllowed was similar to that used by Pines and Ipatieff [48] in the preparation of *tert*-butyl*cyclo*pentane.



m-Xylenol-(3 : 5-dimethylphenol) distilled at 125°/22 mm and melted at 64°. It was reduced catalytically in 600-g batches with Raney nickel and hydrogen at 160° to 180° and 60 to 80 atm to 3 : 5-dimethyl*cyclo*hexanol, b.p. 82°/14 mm. The refractive index, n_D^{20}, for several batches varied between 1·4554 and 1·4560. von Braun and Haensel,[49] who used more drastic conditions of reduction, obtained a product of n_D^{20} 1·4546, containing probably a different proportion of *cis* and *trans* forms.

From our mixture one form of 1 : 3-dimethyl*cyclo*hexanol of m.p. 39° could be isolated by crystallization [50] from acetone at −40°, and this may have been identical with a form of m.p. 41° isolated by von Braun and Anton.[51]

α, γ-*Dimethyladipic Acid.*

The mixed dimethyl*cyclo*hexanol was oxidized in batches of 100 g by dropping into a mixture of nitric acid (400 cc of D 1·42) and water (200 cc) kept at 60°. Evaporation of the nitric acid left a thick oil, which on long

standing deposited a small quantity of crystals, m.p. 68°. (Found : C, 55·1 ; H, 8·2 per cent. Mol. wt. (by titration) 174. Calc for $C_8H_{14}O_4$, C, 55·1 ; H, 8·1 per cent ; mol. wt., 174.)

2 : 4-*Dimethyl*cyclo*pentanone*.

The viscous adipic acids were cyclized by heating with 10 per cent of the weight of crystalline baryta. Ketone began to distil when the temperature reached 215°, but most distilled at 245°. After the distillate had been washed with alkali, with water, and dried, it distilled at 152° to 154°. (Yield 75 per cent of the theoretical.)

2 : 4-*Dimethyl*cyclo*pentanol*.

The ketone reduced smoothly to the secondary alcohol, b.p. 98° to 99°/70 mm, 58°/10 mm. Dehydration was effected by passage over alumina at 300°. The crude 1 : 3-dimethyl*cyclo*pentene distilled at 80° to 95°, mainly at 90° to 95°.

1 : 3-*Dimethyl*cyclo*pentane*.

Reduction of the crude dimethyl*cyclo*pentene with Raney nickel and hydrogen at 80° to 140° and 80 atm gave a product which began to boil at 85°, but most passed over at 90° to 92°, all portions of this main fraction having n_D^{20} 1·4099 ± 0·0002.

A.P.I. Tables give for *trans*-1 : 3-dimethyl*cyclo*pentane b.p. 90·97° and n_D^{20} 1·4088.

T. H. B. B. E.
T. S. M. J. C. S.
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n-Propyl*cyclo*pentane.

This hydrocarbon has been prepared from *cyclo*pentanone *via* *n*-propyl-*cyclo*pentanol. About 10 litres of *n*-propyl chloride were prepared in a semi-continuous process by the action of hydrogen chloride and zinc chloride on the alcohol. The propyl chloride, distilled from phosphorus pentoxide, boiled at 46° to 47°.

n-*Propyl*cyclo*pentanol*.

Magnesium (110 g) was placed in a 3-litre, three-necked flask along with 300 cc of ether, and a solution of *n*-propyl chloride (350 cc) in ether (500 cc) was added during 1½ hr.

The solution of the Grignard reagent was then cooled (ice + salt) and *cyclo*pentanone (336 g or 354 cc) in ether (500 cc) was added during 2½ hr. After the addition the mixture was stirred at room temperature and then left overnight. Decomposition with water and then with dil sulphuric acid gave two clear layers. Working up in the usual way gave 350 g (70 per cent yield) of the tertiary alcohol, b.p. 75°/18 mm.

n-*Propyl*cyclo*pentane*.

The tertiary alcohol was dehydrated by refluxing for 2 hr with 0·5 per cent of its weight of iodine, followed by slow distillation through an all-glass Dufton column. The upper layer of the distillate was washed with dil sulphur dioxide solution, with alkali, and dried over magnesium sulphate. In order to remove halides the olefin was refluxed with sodium and then distilled. Each 350 g of alcohol gave 240 to 260 g of olefin fraction, b.p. 130° to 132°. The olefin hydrogenated rapidly at 60° with 50 atm of hydrogen in presence of Raney nickel. For the removal of traces of olefin the product was shaken with 2 per cent permanganate solution, washed, dried with sodium sulphate, and then distilled from sodium. (In later preparations of hydrocarbons higher temperatures and pressures were used in the hydrogenation, so that the products were stable to dil permanganate solution in a 24-hr test, and the treatment of the bulk with permanganate could be omitted.) The 2½ litres of *n*-propyl*cyclo*pentane thus prepared boiled at 130·20° to 130·24°/748 mm and had n_D^{20} 1·4266.

Chavanne [52] gives b.p. 130·8°/760 mm, n_D^{20} 1·4265, and Doss [30] gives b.p. 130·8°; n_D^{20} 1·4266.

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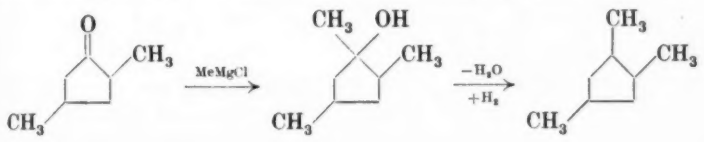
1 : 2 : 4-Trimethyl*cyclo*pentane.

The 2 : 4-dimethyl*cyclo*pentanone required for this preparation was made as described in the synthesis of 1 : 3-dimethyl*cyclo*pentane.



1 : 2 : 4-*Trimethyl*cyclo*pentan*-1-*ol*.

48 g (2 g atoms) of magnesium were placed in a 2-litre, three-necked flask fitted with a stirrer, a lead-in tube, and a reflux condenser. Methyl chloride was passed in until all the magnesium dissolved; the flask was then cooled in ice and a further 200 cc of ether was added. 224 g (1·9 mol) of the dimethyl*cyclo*pentanone in 400 cc of ether were then slowly run in from a tap-funnel; when all the ketone had been added, the mixture was refluxed gently and finally allowed to stand overnight. Decomposition of the Grignard complex and working up in the usual manner gave a crude product, b.p. 90° to 100°/90 mm. Redistillation at 773 mm gave 170 g of trimethyl*cyclo*pentanol, b.p. 155° to 156° (yield 60 per cent).

1 : 2 : 4-*Trimethyl*cyclo*pentane*.

570 g of trimethyl*cyclo*pentanol, when passed over alumina at 320°, gave a green liquid smelling of mercaptans (from the sulphate present in the alumina). Washing with sodium hydroxide solution removed the smell, and the dried olefin gave a main fraction of b.p. 105° to 118° (327 g), n_D^{20} 1·4366. Reduction of this fraction with Raney nickel and hydrogen at

160° and 80 atm gave a product which on distillation behaved as if it was a mixture of most or all of the four possible geometrical isomerides :—

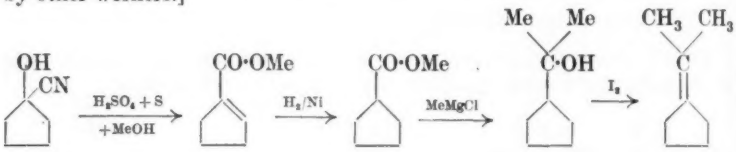
Fraction.	B.p., ° C/744 mm.	Volume, cc.	n_D^{20}.
I	100 to 107	25	—
II	107 to 110	25	1·4128
III	110 to 111·6	30	1·4132
IV	111·6 to 112·6	50	1·4135
V	112·6 to 113·2	50	1·4142
VI	113·2 to 114·0	30	1·4149
VII	114·2 to 115·1	50	1·4153
VIII	115·1 to 116·1	70	1·4169

Zelinsky,[53] who started from a specially pure specimen of *d*-pulegone, obtained a sample of 1 : 2 : 4-trimethyl*cyclo*pentane of b.p. 112·5° to 113°, n_D^{20} 1·4156.

S. H. M.

*iso*PROPYLIDENE*cyclo*PENTANE.

This olefin was made during the exploration of a route to *iso*propyl*cyclo*pentane. [The reaction between *iso*propyl magnesium chloride and *cyclo*pentanone yields mainly *cyclo*pentylidene*cyclo*pentanone (Meerwein [39]), and another route *via cyclo*pentadiene and dimethylfulvene was being used by other workers.]



cyclo*Pentanonecyanhydrin*. (Wislicenus and Gärtner.[54])

Conc hydrochloric acid (1·1 mol) was slowly added with vigorous stirring to an ice-cold mixture of *cyclo*pentanone (1 mol in 4 times its vol of ether) and powdered potassium cyanide (1 mol). The ether layer was removed and the aqueous layer extracted twice with ether, giving the cyanhydrin, b.p. 118° to 120°/25 mm, in 80 per cent yield.

*Methyl*cyclo*pent*-1-*en*-1-*carboxylate*.

(Compare the I.C.I. patent,[40] for the preparation of methylmethacrylate from acetone cyanhydrin.) Conc sulphuric acid (3 mol) was added during 1 hr to a well-cooled and stirred mixture of *cyclo*pentanone cyanhydrin (2 mol) and sulphur (5 g). The mixture was heated at 60° to 70° for ½ hr and then at 120° for 1 hr. After cooling, a mixture of methyl alcohol (4 mol) and water (4 mol) was added and the whole was heated in an oil-bath at 110° for 15 hr. Addition of saturated salt solution (760 cc) to the cooled mixture precipitated an oil which, isolated with the aid of ether, boiled at 70°/25 mm (yield 56%). (Found : C, 66·2; H, 8·1. Calc for $C_7H_{10}O_2$: C, 66·7; H, 7·9%.)

*Methyl*cyclo*pentane Carboxylate*.

The unsaturated ester reduced with Raney nickel and hydrogen at 30 atm in the cold gave a quantitative yield of liquid, b.p. 158°/762 mm,

n_D^{20} 1·4363. (Found: C, 65·5; H, 9·4. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4 per cent.)

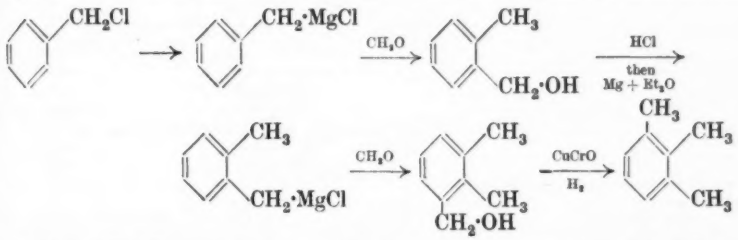
cyclo*Pentyldimethyl Carbinol.*

Methyl*cyclo*pentane carboxylate (64 g, 0·5 mol) was slowly added with vigorous stirring to the cooled Grignard reagent prepared from methyl iodide (213 g, 1·5 mol) and magnesium (36 g, 1·5 g atom) in dry ether (750 cc). The resulting carbinol (50 g, 75 per cent yield) was dehydrated by heating with 0·25 g of iodine at 140° for ½ hr, followed by slow distillation. The product, freed from iodine and distilled from sodium, boiled at 132·5°/755 mm, and had n_D^{15} 1·4535 (yield 90 per cent). (Found: C, 87·2; H, 12·5. Calc for C_8H_{14}: C, 87·3; H, 12·7 per cent.)

T. H.

1 : 2 : 3-Trimethylbenzene (Hemimellitene).

L. I. Smith and Spillane [55] prepared a large quantity of this hydrocarbon by the method of Tiffeneau and Delange.[56] In our preparation the reduction



of the $-CH_2OH$ group in 2 : 3-dimethylbenzyl alcohol was effected by conversion to the iodide and reduction of this with zinc dust and acetic acid.

638 g of benzyl chloride (5 mol, b.p. 178°), 132 g (5·5 g atoms) of magnesium, 2000 cc of ether, and 225 g of paraformaldehyde (dried with phosphorous pentoxide) gave, by the process of Smith and Spillane, approx 300 g (50 per cent yield) of 2-methylbenzyl alcohol, b.p. 135° to 137°/46 mm and m.p. 35·5°. The chloride derived from this alcohol gave by the Tiffeneau rearrangement only a 30 per cent yield of 2 : 3-dimethylbenzyl alcohol, b.p. 129° to 131°/25 mm, m.p. 64·5°. Crystallized from light petroleum it melted at 65·5°. (Smith and Spillane [55] obtained a 48 per cent yield of alcohol, m.p. 65° to 66·5°.)

An attempt to reduce the $\cdot CH_2OH$ to $\cdot CH_3$ via the chloride and the Grignard reagent, $Br\cdot CH_2MgCl$, led by a Wurtz reaction to a solid of m.p. 108·5° to 109°, which gave analytical figures corresponding to *sym*-di(2 : 3-dimethylphenyl)ethane. (Found: C, 90·5; H, 9·2%. $C_{18}H_{22}$ requires C, 90·8; H, 9·2 per cent.) The other product was a liquid, b.p. 172° to 176°/755 mm., n_D^{20} 1·5122, which was impure hemimellitene.

Reduction of 2 : 3-*dimethylbenzyl Iodide.*

As the chloride had already been prepared, it was converted into the iodide by the Finkelstein [57] reaction. 100 g of sodium iodide (0·66 mol)

were dissolved in 500 cc of dry acetone. When 37 g (0·24 mol) of 2 : 3-dimethylbenzyl chloride were added the mixture quickly became cloudy, and sodium chloride was deposited. The mixture was heated under reflux for 30 min, and then 350 cc of acetone were distilled off (using a draught chamber, as the iodide is a powerful lachrimator). Addition of the residue to water produced a dark oil which was isolated with the aid of ether, but was not purified. 24 g of this crude iodide were then dissolved in 200 cc of glacial acetic acid and zinc dust in small portions to the warm solution; finally the mixture was boiled under reflux until a test showed that no organic iodide remained (cf. Carey and Smith [58]). Fractionation of the product gave hemimellitene, b.p. 174·7° to 176·2°/755 mm, f.p. −25·5°, n_D^{20} 1·5134. Smith and Spillane [55] give b.p. 176·2°/760 mm, m.p. −25·4°, n_D^{20} 1·5130. Mair and Schicktanz [59] give m.p. −25·47° for hemimellitene isolated from Oklahoma petroleum. A.P.I. Tables give b.p. 176·15° and n_D^{20} 1·5139.

E. R. W.

Collected Table of Physical Properties.

Hydrocarbon.	n_D^{20}.		B.p., ° C/760 mm.	
	This work.	A.P.I. Project 44, selected values 1945.	This work.	A.P.I. Project 44, selected values 1945.
Heptanes.				
2-Methylhexane	1·3850	1·38490	90·1	90·05
3-Methylhexane	1·3887	1·38865	91·6	91·95
3-Ethylpentane	1·3934	1·39340	93·35	93·468
2 : 3-Dimethylpentane	1·3920	1·39200	89·65	89·79
2 : 4-Dimethylpentane	1·3822	1·38150	80·50	80·51
Octanes.				
2-Methylheptane	1·3950	1·39495	117·4	117·645
3-Methylheptane	1·3983	1·39849	118·6	118·927
4-Methylheptane	1·3980	1·39792	117·5	117·712
3-Ethylhexane	1·4018	1·40162	118·5	118·537
2 : 3-Dimethylhexane	1·4012	1·40138	115·5	115·61
2 : 4-Dimethylhexane	1·3954	1·39534	109·2	109·43
2 : 5-Dimethylhexane	1·3929	1·39246	109·0	109·16
2-Methyl-3-ethylpentane	1·4041	1·40402	115·4	115·653
2 : 2 : 3-Trimethylpentane	1·4030	1·40295	110·1	109·846
2 : 3 : 4-Trimethylpentane	1·4043	1·40195	113·3	113·47
Nonane.				
2 : 3 : 5-Trimethylhexane	1·4053	1·4060	130·9	131·37
Decanes.				
4-*iso*Propylheptane	1·4155	—	158·9	—
2 : 3-Dimethyloctane	1·4146	—	164·7	—
4 : 5-Dimethyloctane	1·4185	—	162·0	—
Cyclic.				
*cyclo*Pentane	1·4068	1·40645	49·3	49·264
1 : 2-Dimethyl*cyclo*pentane (*cis*)	1·4212	1·4221	99·3	99·25
1 : 2-Dimethyl*cyclo*pentane (*trans*)	1·4119	1·4120	91·8	91·89
1 : 3-Dimethyl*cyclo*pentane	1·4099	1·4088	90–92	90·97
n-Propyl*cyclo*pentane	1·4266	—	130·75	—
1 : 2 : 3-Trimethylbenzene	1·5130	1·5139	176	176·15

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OBITUARY.

ARTHUR TETLEY BEAZLEY, M.B.E.

ARTHUR TETLEY BEAZLEY, M.B.E., B.Sc., B.Eng., A.M.Inst.C.E., F.Inst.Pet., died on July 19, 1949, after a short illness. Through his passing the Institute has lost one of its Original Members, the petroleum industry one of its pioneers, and his colleagues an able and charming personality.

Born in 1881 the third son of James Henry Beazley of Birkenhead and Liverpool, Arthur Tetley was educated at Bilton Grange Preparatory School, Malvern College, and Liverpool University, where, in 1902, he graduated B.Sc., and B.Eng., with first-class honours. Specializing on the electrical side he served his apprenticeship at Rugby with the British Thomson-Houston Company.

In 1904, to obtain further experience, he crossed to the United States, where he joined the General Electric Company, Schenectady. Continuing his work on electrical engineering he later specialized further on railway motors. In 1907, for health reasons, he travelled west to California, where he joined the Northern Electric Company.

These early days saw the rise of the petroleum industry in the United States, and California was one of its nurseries. It was thus not surprising that a young skilled engineer with the broad basic training of Arthur Beazley was attracted to this new industry. In 1909 he joined, as field engineer, the California Oilfields, Ltd., a company controlled at that period by Messrs. Balfour Williamson & Co. Control later passed to the Shell, and the oilfields concerned constituted their first petroleum production interest in the U.S.A. Arthur Beazley continued his work under this new management having, in 1911 at the age of thirty, risen to the responsible position of field manager.

The writer is indebted to Mr Stephen Foot for accurate detail of an incident during this period illustrative of Arthur Beazley's ability :—

> " In January 1914 I was Manager of the Corona Petroleum Co., a subsidiary in Mexico of the Royal Dutch/Shell interest. On January 11 we struck in the Panuco field a gusher which has been estimated as the third largest oil well in the history of oil exploration.
>
> " It started flowing at the rate of 25,000 tons per 24 hours and maintained an astonishing flow over a period of nearly twenty years.
>
> " The gate valve at the casinghead was damaged by the drilling tools that were shot into the air when the oil was first struck and the well could not be brought under control by normal methods.
>
> " I received a cable from London to say that they had arranged with the Shell Company of California to send to our assistance one of their field managers, Mr Beazley. He arrived in the course of the next few days and was a great help to us in making secure and lasting arrangements for controlling the flow of oil from the well."

At the outbreak of the 1914 war Arthur Beazley immediately returned to England to enlist as a private in the Kings (Liverpool) Regiment.

Within a few months he had risen to the rank of Captain. Crossing to France in 1915 with his regiment he commanded a Company. Later, in view of his scientific qualifications, he was recalled to England to take up a position with the Ministry of Munitions. For his work with them he was awarded the M.B.E.

In 1919 he rejoined the Shell and visited for them Hong Kong, Japan, Singapore, and Sarawak before taking up an appointment in Mexico as field manager for the Mexican Eagle Oil Co., where a few years later he became general manager.

In 1926 he returned to the Balfour Williamson interests as technical adviser to Lobitos Oilfields, Ltd., and Anglo-Ecuadorian Oilfields, Ltd., to become a year later general manager and in 1945 a director of both companies. During this period he was instrumental in the building of a full-scale refinery by Lobitos Oilfields, Ltd., in Cheshire, England. His keen interest and progressive outlook contributed largely to its success.

From the time of their formation he was a member of the Lubricating Oil Committee of the Petroleum Board and a member of the Post-war Petroleum Advisory Committee.

Arthur Beazley was one of the small band who agreed to join the Institute prior to its actual formation. In 1913, on its formation, he was elected a Member. In 1939, on the institution of that grade, he was elected a Fellow. In 1947 he was elected a Member of Council and became an active member of the Finance Committee until his resignation a few months prior to his death.

Arthur Beazley was exceptional in possessing the easy charm, courtesy, and high integrity generally associated with earlier years combined with a modern outlook. He had a firm grasp of the techniques of both petroleum production and petroleum refining, and was ever keenly interested and receptive of improved methods or technical advances. To staff and employee he became a father who guided, supported, and, on occasion, chastised. By the very trust which he placed in others he inspired a high degree of respect, trust, and high endeavour.

A Memorial Service was held in London on August 9, at which the Institute was represented by its President Mr E. A. Evans, Col. S. J. M. Auld, Mr R. R. Tweed, Mr J. S. Parker, and the editor, Mr George Sell.

J. S. P.

WILFRED HERMANN HOFFERT.

It is with deep regret that we announce the untimely death, on August 1, 1949, of Wilfred Hermann Hoffert, chief chemist of the National Benzole Company, Ltd., who joined the Institute in 1934 and became a Fellow in 1939. He is survived by his wife, three sons, and three daughters.

Born on January 29, 1892, the son of one of H.M. Inspectors of Technical Schools, he was brought up in a scientific atmosphere. At an early age he was familiar with some of the classic scientific curiosities, such as the Whimshurst machine and Lissajou's figures. It is not surprising, therefore, that he should eventually embrace a scientific career.

He attended Whitgift School and Manchester Grammar School. Early

in his school career he took little interest in his studies, and it was not until his father had had a serious talk with him that he settled down to solid work. In 1911 he was awarded an open natural-science exhibition to Jesus College, Oxford, gaining the degree of B.A., with first-class honours in natural science (chemistry) in 1914, also being awarded a research scholarship at Jesus College in the same year. During his stay at Oxford he rowed for his college.

In August 1914 he was commissioned in the Manchester Regiment, being wounded at Suvla Bay in 1915. The following year saw him Area Gas Officer attached to Headquarters Staff at the Machine Gun Training Centre. He then became a " founder member " of the Aeroplane Experimental Station at Martlesham Heath, formed under Sir Henry Tizard in 1917. He was promoted first-class Experimental Officer, with the rank of Captain, in August 1918, and visited the Section Technique, Paris, to study French methods of testing aeroplanes, and also joined the British Aviation Mission to America, where he was attached to the Headquarters Staff at the Wilbur Wright Experimental Aviation Field, Dayton, Ohio.

From 1917 to 1920 he held a Salter's Fellowship at Jesus College, Oxford, working under D. L. Chapman, F.R.S., on the subject of the systematic chlorination of the aromatic hydrocarbons. A paper on this subject was submitted to the Chemical Society jointly with C. G. Harris. He was awarded his M.A. degree in 1919, and B.Sc. degree in 1920.

In 1920 he held a temporary tutorship in chemistry at Christ Church, Oxford, and in the same year was appointed senior research chemist to Messrs Bowdler and Bickerdike at Church, Lancs., a post which he held until January 1922, when he took up a temporary engagement at H.M. Fuel Research Station, Greenwich. Whilst he was with Messrs. Bowdler and Bickerdike he worked on the subject of the determination of phenol in mixtures of tar acids, the results of this work being published in the *Journal of the Society of Chemical Industry* in 1922.

In November 1923 he was appointed research chemist of the Joint Research Committee of The National Benzole Association and the University of Leeds. In 1929 the Association severed its official connexion with the University, and he became chief research chemist to the Association. In 1935 the technical and research work carried out by the Association was unified with the technical control exercised by the National Benzole Co., Ltd., and Hoffert became chief chemist, supervising these joint technical activities.

Hoffer will be remembered chiefly for his services to the benzole industry, and his numerous papers, published alone and jointly with members of his staff, have had a considerable influence on lifting the production and refining of benzole from rule-of-thumb to scientific control.

" Motor Benzole, its Production and Use," published in 1931 conjointly with G. Claxton, and revised in 1938, is, apart from an excellent little book published in 1920 by Whitehead entitled " Benzol, its Recovery, Rectification and Uses," the only book in English devoted solely to the production of benzole. This book was begun chiefly because the tenancy of the laboratories at Leeds University had ceased in December 1929, and the new ones being built at Willesden were not ready for occupation until late spring, 1930. One of Hoffert's last tasks was to revise thoroughly and

bring up to date a part of the chapter in this book dealing with physical properties.

Hoffert's earlier work for The National Benzole Association consisted of a characteristically thorough examination of the adsorptive capacity of active carbon and silica and other metal oxide gels, which were then being tried as media for benzole recovery from coal gases. Accounts are also given of visits to both Germany and the United States to examine plant erected for the recovery of benzole by adsorbents.

In 1926 the research work of the Joint Benzole Research Committee was directed towards means of preparing a motor fuel without the destructive elimination of unsaturated hydrocarbons by sulphuric acid. The use of ultra-violet light was adopted as a means of hastening the resinification process of the unsaturated hydrocarbons. Hoffert noticed that whereas some samples gave only a small deposit of dark-coloured resin, others gave a voluminous residue of pale-coloured gum. From this carefully noted fact was evolved the Inhibitor Process, in which traces of phenols and other substances are deliberately added to motor fuels to prevent the oxidation of unsaturateds. This process, which was patented in 1926, was at first viewed somewhat cautiously by the benzole industry, but since 1929, when the specification for motor benzole was altered to permit the manufacture of inhibited benzoles, there has been an annual saving of benzole exceeding, at its maximum, 1¾ million gal.

Also, during the Leeds days, Hoffert carried out a series of careful determinations of the absorptive capacity of a number of typical benzole wash oils.

From 1930 onwards he became less actively associated with actual laboratory work, but his character, particularly his unfailing attention to detail and to the careful checking of facts, impressed itself upon his staff. More and more of his time was devoted to the commercial aspects of scientific work and to serving on many committees, among which may be mentioned :

Research Committee, The National Benzole Association.
Specifications Committee, The National Benzole Association.
Crude Benzole Evaluation Committee, National Benzole Co. Ltd.
Standardization of Tar Products Test Committee
Sub-Committee No. 3, and various panels, of the Institute of Petroleum.
Benzole Technical Committee of the Ministry of Fuel and Power, of which he was chairman.

His published work during this period became more documentary in character. Most of the papers of this kind were due entirely to his inspiration, but it was characteristic of his complete unselfishness that he seldom took sole credit for them. The annual "Summary of Papers and Patents of Interest to the Benzole Industry," published by The National Benzole Association since 1934, was always close to his heart. This valuable document was based on a careful system of abstracting, all abstracts being recorded on a card index. This system was commenced as soon as he joined the organization, and now contains at least 50,000 cards.

His written English was characteristic of the man. Precise, it never contained those oratorical twists that might have been useful when

attempting to convey to non-technical associates one of those intangible points that were obvious enough to his technical colleagues. He was ill at ease with this type of writing and disliked it. But his scientific papers were models of clear, incontrovertible statement. Tables were neat, carefully set out, and complete in detail. Documentation of all papers with which he was associated was very full, and he insisted on a high standard of accuracy, references being checked at all stages in the preparation of a paper. If at times he was over-cautious in his statements, or used the conditional too frequently, he likewise frequently saved his younger and more headstrong colleagues from the distasteful task of "eating" their own words.

Of the man—he was modest and shy. He knew many people, but was known by a few. His integrity and complete unselfishness made him loved by all of those who worked with him. Above all, his capacity for concentration and hard work placed him in a superior mental class.

"He did the work he was called to do without complaint, and no one could doubt but that what he said he meant, and what he did he did to good purpose."

G. C.

ARTHUR GILBERTSON HUTCHISON.

Dr A. G. Hutchison's many friends will have learned with regret of his accidental death while on holiday at Tenby, South Wales.

Arthur Gilbertson Hutchison was born in Aberdeen on August 12, 1902. He was educated at Aberdeen University and obtained his B.Sc. in Geology in 1926. For the next twelve months he continued to carry out research work at Aberdeen University, and in 1927 he went to Cambridge, attached to the Sedgewick Museum as research assistant, where in 1929 he was awarded a Ph.D.

In September 1929, Dr. Hutchison joined the Geological Department of The Royal Dutch/Shell Group, and with the exception of a few months in 1932, when he held an appointment at Cambridge University under Professor Tilley, he remained with this firm throughout his career.

During this time he served in British Borneo, Trinidad, B.W.I., and the head offices in both London and The Hague.

From April 1948 until May 1949 he travelled in South America as a special consultant in technical as well as organization matters in connexion with petroleum exploration. After his return from South America and before resuming his duties at The Hague office, Dr Hutchison was on holiday in South Wales when he met his tragic death on the cliffs of Pembrokeshire.

All through his career with the Group, Dr Hutchison retained the highest level of professional competence, his outstanding tact and quiet friendly manner endeared him to all his colleagues and to everybody who came in contact with him. His particular interest in the welfare of his subordinates gained him the greatest respect. Together with his well-recognized ability in organizing, this quality made him an ideal exploration leader.

A great deal of Dr Hutchison's leisure time was spent in fishing, a sport in which his profession allowed him to indulge throughout his career.

A Personal Note by a Member Friend.

As recorded in the foregoing Dr Hutchison spent some three years in Trinidad, and it was here that he was best known to a wide circle of Institute of Petroleum members. He was an enthusiastic and clear-minded observer of geological subjects in that Island, and his views were always held in high esteem by his fellow geologists. As long as geologists foregather in Trinidad it will be remembered that it was he who discovered the first undoubted Jurassic ammonite in Trinidad's northern range. "Hutch," as he came to be known, had a ready wit and a most happy disposition which made him many friends. His wide experience and natural aptitude for his science had already carried him far, and there is no doubt that, but for the lamentable accident which caused his death, he would have become a leader amongst petroleum geologists.

E. C. S.